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(6) ANNUAL TECHNICAL PROGRESS REPORT

FOR 1975/76.

(11) 1976 (13) 170 p.

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MAR 3 1978
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Materials Science Center of Cornell University
Ithaca, New York

(15) N00014-75-C-1109, ARPA Order-3010

During this period the Materials Science Center received support from the National Science Foundation under Grant DMR72 03029 and the Advanced Research Projects Agency, under ARPA Order No. 3010, monitored by the Office of Naval Research under Contract No. N00014-75-C-1109.

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INTRODUCTION

The Materials Science Center (MSC) is the focus of an interdisciplinary research program which encompasses the research activities of approximately fifty faculty members from the fields of Applied Physics, Chemistry, Electrical Engineering, Materials Science and Engineering, Theoretical and Applied Mechanics and Physics. Approximately one half of the Center membership is from each of the Colleges of Arts and Sciences and of Engineering.

MSC was founded in 1960 with financial support from the Advanced Research Projects Agency, with the twin objectives of intensifying research and expanding graduate education in materials science, with emphasis upon the interdisciplinary character of this rapidly evolving field. On July 1, 1972 funding of the Center came under the auspices of the National Science Foundation, administered by the Materials Research Laboratory section of the Division of Materials Research. Substantial additional financial support was received from a grant to the Center by the Advanced Research Projects Agency, and from grants to individual members by federal agency, foundation, and University sources. This continued support is gratefully acknowledged.

An Executive Committee consisting of both elected and ex officio members develops the policies of the Center and allocates resources to the Central Facilities and the research programs of the Members. In 1975-76 the members of this committee were:

Voting Members

S. H. Bauer, Department of Chemistry
W. D. Cooke, Vice President for Research, Chairman
E. T. Cranch, Dean, Engineering
R. Hoffmann, at large, College of Arts and Sciences
H. H. Johnson, Director, Materials Science Center
D. C. Knapp, Provost
E. J. Kramer, Materials Science and Engineering
H. Levin, Dean, Arts and Sciences
A. L. Ruoff, at large, College of Engineering
A. J. Sievers, Department of Physics
J. Silcox, Applied and Engineering Physics

Invited Non-Voting Members

R. W. Balluffi, Director, Materials Science and Engineering
B. W. Batterman, Director, Applied and Engineering Physics
M. E. Fisher, Chairman, Department of Chemistry
W. W. Lambert, Dean, Graduate School
R. M. Littauer, Chairman, Department of Physics
Y. H. Pao, Director, Theoretical and Applied Mechanics
G. F. Rankin, Associate Director, Materials Science Center
T. R. Rogers, Director, Office of Academic Funding
R. H. Silsbee, Director, Laboratory of Atomic and Solid State Physics

This 1975-75 report consists of two principal sections plus an index. Section I describes accomplishments in the research program of the Center in terms of the Study Group concept. Included is a condensed account of the research activities of each member of the Center, and listings of graduate students, postdoctoral associates, publications, and sources of financial support. Section II describes the activities of each of the Central Facilities in 1975-76, with emphasis upon new developments.

I. RESEARCH PROGRAM

The MSC structure for organizing and focussing the research program is the Study Group system. It was instituted following a careful study of the way in which MSC should organize itself to respond to the research environment of the 70's. The twin objectives were to devise a system which would foster interdisciplinary and interactive research in a systematic way, and yet retain ample flexibility such that MSC could continue to respond rapidly to newly perceived scientific opportunities.

A Study Group is an affiliation of MSC with a significant commitment to a research area of major interest to the Center's overall research program, such as Mechanical Properties, Phase Transitions, Surface Science, etc. Study Group membership frequently cuts sharply across departmental boundaries, because of the interdisciplinary and interactive nature of much of modern materials research. Occasionally a faculty member will be formally affiliated with more than one Study Group. This tends to occur either with theorists with wide ranging interests, or with experimentalists whose individual research programs are built around techniques or equipment applicable to problems in more than one Study Group area. This flexibility is essential to a dynamic materials research effort, and is easily incorporated in the Study Group system.

The Study Groups provide planning and coordination through group discussion for the research activities within their respective areas. An important aspect is to recognize and develop areas within each Study Group where two or more members can concentrate their efforts in an interactive mode. Typical and not exhaustive examples are the grain boundary research in the Defect Structures Group, grain matrix deformation studies in the Mechanical Properties Group, and the combined experimental and theoretical study of the low temperature phases of helium in the Phase Transition Study Group.

The Study Groups also develop proposals for the initiation or major expansion of central facility capabilities, and for the acquisition of major equipment. Broad-based equipment needs often first become evident in Study Group discussions. Final decisions on allocation of resources of course remain with the Director and the Executive Committee, but Study Group proposals and views have become a significant influence on the decision-making system.

The Study Group environment does encourage in a natural way the development and extension of interactive and interdisciplinary research. In addition to the activities described above, several of the Study Groups either conduct or support active seminar programs. Both collaborative and individual projects are supported within a given Study Group, with an increasing emphasis upon the collaborative and interactive mode. Some individual projects are also supported under Exploratory and Continuing Programs.

MECHANICAL PROPERTIES STUDY GROUP

Over the past few years the research program of this Study Group has both grown and become more focussed. Significant efforts are now underway in the area of non-destructive testing, grain matrix deformation processes, grain boundary deformation and fracture processes, and flaw tip processes. The non-destructive testing (NDT) area has been developed from essentially a zero base to a very significant experimental effort using ultrasonic pulse spectroscopy, holographic interferometry, and acoustic emission. Some of these techniques, especially acoustic emission, are about to be applied in other areas of the Study Group. The experimental NDT program is accompanied by two significant theoretical efforts, one based in Physics and the other in Theoretical and Applied Mechanics.

The Grain Matrix Deformation area continues to build on the continuing success of the mechanical equation of state approach. A phenomenological model of the processes described by the mechanical equation of state is under development, which may point the way to a better understanding of the microscopic processes. However, the mechanical equation of state is quite useful in its present form for engineering design purposes. Significant interactions have developed between MSC investigators and T&AM faculty who are attempting to develop analytical and numerical design techniques employing mechanical equation of state concepts.

A new project has been started to evaluate the usefulness of mechanical equation of state concepts in describing the high-pressure creep deformation of ceramics. Possible areas of application include analysis of hot pressing processing techniques and of deformation of mantle materials in the earth. This project will make full use of the high pressure expertise present in the Center. As an adjunct the plastic deformation of ultrahard ceramic materials at room temperature is under study with a unique high pressure technique.

Within the past year a new area of Grain Boundary Deformation and Fracture Processes has developed. Building on existing experimental work on grain boundary sliding in metals and theoretical modelling of diffusion controlled grain boundary void growth under stress, new projects have been started on grain boundary crack initiation/damage in creep-fatique loading of ceramics (hot pressed silicon nitride) and metals (stainless steels). Environmental effects are under study both in the creep-fatigue problem and in a program to characterize hydrogen attack at grain boundaries in steel (methane bubble attack).

In the flaw tip processes area the emphasis upon crazing at crack tips in glassy polymers continues, but new efforts have been initiated on crack tip deformation processes in metallic glasses and on slow crack growth in metals at elevated temperatures. In the latter a point of interest is whether a slow crack growth model based upon the mechanical equation of state is applicable.

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Mechanical Properties Study Group Membership

D. G. Ast, Materials Science and Engineering
(for report see New Solid State Materials Study Group)
H. D. Conway, Theoretical and Applied Mechanics
H. H. Johnson, Materials Science and Engineering
D. L. Kohlstedt, Materials Science and Engineering
E. J. Kramer, Materials Science and Engineering
J. A. Krumhansl, Department of Physics
(for report see New Solid State Materials Study Group)
C.-Y. Li, Materials Science and Engineering
Y.-H. Pao, Theoretical and Applied Mechanics
R. Raj, Materials Science and Engineering
A. L. Ruoff, Materials Science and Engineering
W. H. Sachse, Theoretical and Applied Mechanics

H. D. CONWAY, Professor, Department of Theoretical and Applied Mechanics

Research Assistant:

L-C Lee

Composite Materials Stress and Displacement Analysis

During the year the investigations have largely been concerned with:

(a) Completion of the first phase of the studies of curved laminated shells and bars. The loadings are both mechanical and thermal and the effects of interface conditions are considered.

(b) Two dimensional problems of circular inclusions in a loaded matrix, both inclusion and matrix having arbitrary moduli. Inclusions based both on rectangular and triangular arrays are considered. This simulates the problem of fibers in a loaded matrix, and the bond stresses and effective elastic constants are calculated.

This work is now being extended to more general shaped fiber inclusions such as overlapping elongated fibers.

Research supported by the Materials Science Center.

HIGHLIGHTS

Four articles have been published in the scientific press during the year on laminated shells and bars. The stress distributions and effective elastic constants given therein have already proved valuable to designers and analysts of these kind of structures.

A first report has been written on circular inclusions in a loaded matrix with both triangular arrays. This will be published.

REPORTS AND PUBLICATIONS

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"Bending of Multi-Layered Curved Bars," H. D. Conway, Int. J. Mech. Sci, Vol. 17, 283-291 (1975).

"Bond Stresses and Effective Moduli for a Composite Material Reinforced with Various Arrays of Fibers," H. D. Conway, MSC Report 2689. Submitted for publication.

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Hydrogen in Metals

Hydrogen permeation through iron was studied over the temperature range 300-873°K by an ultra high vacuum, monopole gas analyzer technique. Hydrogen gas input pressures were varied from 0.0043 to 0.62atm and membrane thicknesses from 0.0165 to 0.243cm. Volume diffusion control of the permeation process was demonstrated by the pressure and membrane thickness dependence of the steady st.te flux. The permeation coefficient, with an activation enthalpy found to be 8.1±.4 kcal/mole, was independent of both gas pressure and membrane thickness. At temperatures below approximately 600°K, the effective diffusivity increased with both increasing hydrogen gas pressure and increasing membrane thickness. The transition temperature from classical to anomalous behavior decreases with increasing thickness. Apparent activation enthalpies for diffusion were found to range from 1.6 to 8.2 kcal/mole with the lower values associated with thicker membranes. The results are explicable in terms of volume trapping. A positron annihilation study snowed dislocations to be the most probable, dominant trap species.

In contrast, hydrogen permeation through type 310 austenitic stainless steel, studied over the temperature range 425-873°K, showed no volume trapping effects. However, the membranes, ranging in thickness from 0.0051 cm to 0.013 cm, did show an increase in both effective diffusivity and permeation coefficient with increasing hydrogen gas pressure when surface processes were flux limiting. Once volume diffusion control of the permeation process was established, the dependence of permeation and diffusivity on hydrogen gas pressure was eliminated. The permeation coefficient activation enthalpy was found to be 13.1±.4 kcal/mole while that for diffusivity was found to be 11.2±.45 kcal/mole. However, samples neutron irradiated at a fluence of $10^{17} n/cm^2$ showed anomalous effects in that both effective diffusivity and permeation were reduced in value. These results are explicable in terms of volume processes.

Finally, the hydrogen-deuterium isotopic effect was shown to be non-classical in iron while classical in stainless steel. In the case for iron, the non-classical behavior is confined to the pre-exponential diffusion constant since the activation enthalpy for diffusion is identical within experimental error for both isotopes.

Research supported by the Energy Research and Development Administration and the Materials Science Center.

Cyclic Deformation and Fatigue

The low cycle fatigue saturation stress in Ferrovac-E α-iron was studied using diametral plastic strain ($0.001 \leq \Delta\varepsilon_{dp}/2 \leq 0.0135$) as the control variable. Increasing strain rate ($6\times10^{-5} s^{-1}$ - $4\times10^{-3} s^{-1}$) and decreasing temperature (295°K - 173°K) increased the saturation stress levels. The cyclic work hardening coefficient decreased from 0.18 to 295°K to 0.10 at 173°K. The temperature dependence of both the saturation stress and the strain rate sensitivity, as measured during fatigue

cycling, were similar to that measured during monotonic tensile tests. The temperature dependence of the dislocation velocity index m* was in good agreement with published values from high cycle fatigue and monotonic tensile tests. Values of the saturation stress as a function of temperature, at a constant plastic strain rate and plastic strain amplitude, were consistent with the stress values from the Hart mechanical equation of state approach. For diametral plastic strain amplitude $\Delta\varepsilon_{dp}/2 \geq 0.001$, fatigue cracks initiation appeared to occur at grain boundaries.

Research supported by the Materials Science Center.

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"A Study of Fracture Mechanics," L. K. Lai Tu, Ph.D. Thesis, MSC Report 2600 (1975).

"Gas Phase Hydrogen Permeation Through Ferritic Iron, Austenitic Stainless Steel and Neutron Irradiated Stainless Steel From Near 300°K," N. R. Quick, Ph.D. Thesis, MSC Report 2608 (1976).

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"Hydrogen Problems in Energy Related Technology," J. P. Hirth and H. H. Johnson, Corrosion 32, 3 (1976).

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Physical Properties of Ceramic Materials

My research interests are currently focused on the deformation behavior of ceramic materials. During the past year much of our effort was channeled toward systematically building up a laboratory for the study of the physical properties of ceramic and geologic materials; this project is still far from completion. Yet we have begun to use the transmission electron microscope to study the dislocation structures in deformed TiC single crystals and to examine the vacancy ordering in substoichiometric VC. Possibly the most important advance in our thinking has been the decision to adopt an equation of state approach to the deformation studies. We are preparing Ge polycrystalline samples for initial test on Li's load relaxation rig. We plan to look at both Ge (a "simple" covalent material) and TiC (a much more complex material).

Finally interaction with members of the Department of Geological Sciences has been initiated. Professor J. M. Bird and I have been studying the origin of exceedingly rare minerals (e.g., osmium-iridium alloys) found only in tectonically active areas. These minerals all appear to have high-temperature origins and might, for example, represent primordial condensate materials. This rather controversial research has at present no support monies and is drawing on samples available through the Smithsonian and Cornell's Geological Collection.

Research supported by the Materials Science Center.

HIGHLIGHTS

Under a large range of conditions of great interest in geology, the plastic deformation of minerals proceeds by dislocation mechanisms. A study of the dislocation structures of specimens deformed under known mechanical conditions is a prerequisite for understanding these mechanisms. During the past year we developed a new technique for decorating dislocations in the mineral olivine (see the Science article below) which comprises 75% of the upper mantle, a position of the earth undergoing convective flow. This decoration scheme permits 3D examinations of dislocations in the transmission optical microscope over many square centimeters of sample area in contrast to the few square microns possible in the TEM. An extensive study of the homogenity and characteristic features of the dislocation structure in olivine has been completed. Using the weak-beam technique in the TEM, we have demonstrated that dislocations in olivine dissociate into partials with a spacing of roughly 40Å.

Finally, the arrangement and Burgers vectors of dislocations in deformed grains of the rhombohedral mineral calcite have been studied. As a systematic, monotonic relation between stress and dislocation density would provide an invaluable indicator of stress levels operating in the earth, it is exciting to note that the standard $\sigma \propto \rho^{\frac{1}{2}}$ relation holds over our range of test conditions. Consistent with elastic line energy arguments, the three shortest Burgers vectors operate in calcite; interestingly, only one of these was previously reported from slip trace analysis. Also, none of the exceedingly long (e.g., 34.4Å vs. 5.0Å) Burgers vectors previously suggested in the literature were found.

REPORTS AND PUBLICATIONS

"The Dislocation Structure of Experimentally Deformed Marble," C. Goetze and D. L. Kohlstedt, accepted for publication in Contrib. Mineral. Petrol.

"The Observation of Dissociated Dislocations in Deformed Olivine," J. B. Vander Sande and D. L. Kohlstedt, submitted for publication.

"New Technique for Decorating Dislocations in Olivine," D. L. Kohlstedt, C. Goetze, W. B. Durham and J. Vander Sande, Science, 191, 1045-1046 (1976).

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Flux Pinning in Thin Film Superconductors

Measurements of the pinning force density F_p in superconducting thin films with controlled grain boundary microstructures are to be made. Methods for producing films with grain boundaries normal to the film plane from bicrystal films originally prepared by the pressure welding technique by Schober and Balluffi have the same misorientation angle θ_B and same character (tilt or twist). Such films will be used as a model system for investigating the fundamentals of flux pinning by grain boundaries.

Research supported by the National Science Foundation and the Materials Science Center.

Relation Between Structure and Mechanical Properties of Polymers

The kinetics of craze nucleation and growth from sharp cracks in liquid and gaseous environments are being investigated using optical methods. The emphasis here are on the effects of (and interactions between) the environment, stress intensity factor, temperature and polymer weight. Crazes are important both as a preferred site for crack nucleation and as a source of fracture toughness in glassy polymers.

Research supported by the Materials Science Center.

Mechanical Properties of Crazes

The mechanical properties of crazes including the stress concentration at the craze tip, the strain energy release rate of a growing craze, the craze opening displacement profile and local stress profile are measured using a laser holographic interferometric technique. These properties are related to such structural characteristics of the craze as the molecular orientation, length, diameter and area fraction of primary fibrils bridging the craze thickness. The fracture toughness of the craze also is measured in a standard environment using fracture mechanics methods and correlated with the above structural parameters.

Research supported by the Army Research Office-Durham and the Materials Science Center

Collagen: A Biomaterial

Reconstituted collagen is a possible material for artificial kidney dialysis membranes and drug delivery systems. Small angle x-ray measurements are used to determine membrane pore and collagen fibril sizes in water solution. Stress-strain and crack propagation studies in various environments are also conducted. Present emphasis in the mechanical area is on constructing a

model of the elastic deformation of membrane materials and on characterizing the effects of crosslinking on elasticity and strength.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

It was demonstrated for the first time that the rate limiting step in liquid-induced (solvent) craze growth is the capillary-pressure-driven hydro-dynamic flow of the solvent to the craze tip through the porous craze structure. The growth of a craze from a crack tip was monitored with a time-lapse photography system. The craze was then dried under load, the solvent was reintroduced to the crack tip, and the progress of the liquid front within the craze was followed. The solvent front advanced at exactly the same rate as the original craze growth and renewed growth of the craze did not occur until the liquid front had reached the original craze tip.

It was demonstrated for the first time that the craze growth velocity under dry conditions is profoundly affected by the surrounding gaseous environment at room temperature. Crazes were grown from crack tips under stress conditions characterized by the stress intensity factor K_I for the crack. After increasing markedly at low K_I, the initial craze growth velocity became independent of K_I at higher values. This limited craze velocity v_ℓ is very sensitive to the gaseous atmosphere, e.g. substituting He for N_2 increases v_ℓ by a factor of 6 whereas in a 10m torr vacuum, v_ℓ decreases by a factor o: 5. These results are strong evidence that the rate controlling step for dry craze growth is diffusion of gas molecules in the bulk polymer at the craze top. In strong support of this hypothesis are our recent observations that v_ℓ in N_2 is thermally activated with an activation energy for N_2 gas diffusion in the polymer.

Methods using holographic interferometry have been developed to determine the local stresses borne by crazes growing from crack tips and the sequential strain energy release rates G of growing crazes as a function of craze length. These measurements are believed to be firsts, not only for crazes, but for any type of plastic zone at a crack tip. The rapid increase in G observed just before the craze ceases to grow demonstrates that craze growth criteria based on the concept of a critical total strain energy release rate for growth cannot be correct. In fact, we have shown that it is theoretically possible for a craze, unlike a crack, to release strain energy without growing by a relaxation of the craze fibrils and a corresponding increase in craze opening displacement with time; such a craze would have an infinite G.

Because of the great differences in the mechanical properties of solvent (n-heptane and methanol) crazes in polystyrene observed and reported on last year, an investigation of the structure of these crazes using refractive index measurements, transmission electron microscopy and fractographic analysis of craze fracture surfaces has been completed. N-heptane crazes in thin films exhibit a low number density of thick fibrils whereas methanol crazes consist of a highly interconnected network of fibrils, not unlike the craze structure found in crazes grown in air. The craze structure found in thin films is in agreement with the void content determined from refractive index measurements and with the results from scanning electron microscopy of fracture surfaces of bulk crazes grown with n-heptane and methanol. The results suggest that the structure of solvent crazes is strongly dependent on whether the growth temperature is above or below T_g, the glass transition temperature of the solvent plasticized craze, because independent measurements of T_g in equilibrium swollen polystyrene films give T_g=91°C for methanol but T_g=6°C for n-heptance. If T_g is below the growth temperature, weak crazes are formed with a large void content and during growth thin fibrils break by viscous rupture leaving only a small number of load bearing fibrils. If T_g is above the growth temperature, strong crazes are formed with the fibrils strain hardening as the craze opening displacement increases during growth. Preliminary experiments on the structure and mechanical properties of n-heptane crazes grown at lower temperatures also appear to support this hypothesis.

In the collagen area the emphasis has been on relating the observed properties of collagen

dialysis membranes to the fibril structure as characterized by wide and small angle x-ray scattering. Accurate predictions of κ, the Darcy's law hydraulic permeability, have been made based on measured (SAXS) fibril diameters using a new model. These results are exciting because they open the possibility of designing a membrane to have desired transport characteristics by manipulating its fibril structure.

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"Environmental Effects on the Mechanical Properties of Reconstituted Collagen Hollow Fiber Membranes," R. K. Viswanadham, D. Agrawal and E. J. Kramer, MSC Report 2628 (1976). To be published by J. Polymer Sci.

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"Growth Criteria for Solvent Crazes," E. J. Kramer, H. G. Krenz, and D. G. Ast, MSC Report 2684 (1976). Submitted for publication.

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Postdoctoral Associates:

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F. Huang
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Research Assistants:

J. F. Mancuso
C. W. Cho

Mechanical Behavior and Structural Instability at Elevated Temperatures

Mechanical properties of metals at elevated temperatures are investigated by using the approach of a plastic equation of state. A purpose of this work is to explore the general applicability, of the approach of a plastic equation of state to phenomena other than non-elastic deformation such as fracture. The effects of thermally induced microstructural changes are measured to obtain quantitative information to be used as a part of the required input for mechanical design.

Research supported by the National Science Foundation and the Materials Science Center.

Mechanical Properties of Crystalline Solids

Constitutive relations for non-elastic deformation in crystalline solids are developed by using the load relaxation and work hardening data. The grain boundary sliding is an important process for plastic deformation and is included in this work. Attempts are made to establish the micro-mechanical models for the constitutive relations obtained. A part of the program is involved in the investigation of the stress induced cavity growth at the grain boundary.

Research supported by the Energy Research Development Administration and the Materials Science Center.

Mechanical Equation of State for Non-elastic Deformation and Related Phenomena

Anelastic deformation is measured as a function of time and temperature in load change experiments in specimens of varied thermal-mechanical histories. One of the purposes of this program is to establish phenomenological laws for anelastic deformation. The anelastic deformation from the interest of plastic equation of state is time-dependent-recoverable deformation and is an important part of non-elastic deformation in polycrystalline solids.

Research supported by the National Science Foundation and the Materials Science Center.

Deformation in Type 304 Stainless Steel

The purpose of this work is to establish constitutive relations for non-elastic deformation in Type 304 stainless steel by using the approach of a plastic equation of state. It is intended also to develop the methodology of utilizing these constitutive relations in mechanical design. The validity of the constitutive relations and the design methodology will be tested by experiments on a component such as a bend beam.

Research supported by the Electric Power Research Institute and the Materials Science Center.

HIGHLIGHTS

1. A deformation model based on the plastic equation of state which describes a wide range of non-elastic deformation properties of the grain matrix of a crystalline solid has been confirmed by the load relaxation data on Type 316 stainless steel and nickel.

2. The deformation has been tested for its consistency by comparing the anelasticity data and the load relaxation data of Type 316 stainless steel and nickel.

3. The same deformation model has been found to describe in-reactor creep and deformation well.

REPORTS AND PUBLICATIONS

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Dynamic Stress Analysis of Thick-Walled Reactor Pressure Vessels

This is the last year of a project sponsored by NSF which was initiated in Fall, 1973. The main objective was to develop methods to analyze the transient stresses in a thick-walled cylindrical and spherical pressure vessels used in nuclear power industries. Three methods have been applied: (1) Applying the calculus of residues to determine the transient response from the normal mode analysis. (2) Using the Fast Fourier Transform algorithm to carry out the Fourier synthesis. (3) Extending the method of generalized ray to media bounded by cylindrical or spherical surfaces. The last method which was newly developed by this research group is most effective for vessels with a large thickness. The solution derived by applying this method is exact and numerical results are obtainable with great accuracy.

Research supported by the National Science Foundation, the College of Engineering and the Materials Science Center.

Dynamic Instability of a Loaded Elastic Column

This project investigates the stability of a column with a top weight subjected to vertical dynamic forces. Due to seismic waves, the foundation of a column is excited to move both horizontally and vertically. The effect of the horizontal motion is well known. As shown in this analysis, a vertical motion may also excite the column to vibrate horizontally with large amplitude. Instability of the column may result when the driving frequency equals twice the natural frequencies, or the differences or the sums of any two natural frequencies of the column.

Research supported by the College of Engineering.

Acoustic Pulse Spectroscopy

Two major parts of the research undertaken this year are: (1) The development of a transition matrix for the scattering of elastic waves by a body of arbitrary shape. (2) The development of a theory to interpret the power spectra of elastic pulses scattered by an inclusion in solids. The first part of the research is near completion and a computer code has been developed to calculate the total or differential scattering cross sections of inclusion of an arbitrary convex shape. The second part is completed for the case of scattering by a circular or spherical inclusion (liquid or cavity). The spectra of a liquid inclusion are interpreted on the basis of selective transmission, those of a cavity are on the basis of interference of the reflected and creep waves. This research is a continuation of the joint project with W. Sachse.

Research supported by the National Science Foundation and by the Materials Science Center.

Acoustic Emission

A project to study the basics of acoustic emission used widely in industries for non-destructive testing of materials was initiated this year. The initial phase of the research is to analyze the propagation of ultrasonic pulses in a plate or a cylindrical shell. The purpose is to isolate the original pulse generated by an artificial source in the medium from the influence of multiple reflections at the boundary of the medium, so that one can characterize the nature of the source from the propagating signal.

Research supported by the College of Engineering and the Materials Science Center.

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Fracture in Polycrystralline Materials During Elevated Temperature, Cyclic-Loading Applications

This study of fracture is related to two types of materials, austenitic stainless steels and hot-pressed silicon-nitride, both of which are of commercial interest. The concepts being developed, however, are general and would apply to other materials e.g., superalloys, cladding materials for nuclear fuels such as Zircaloy, and to fracture in nuclear fuels such as uranium carbide. Our objective is to develop mechanistic models for fracture in these materials under conditions of elevated temperature and cyclic loading.

Research supported by the Air Force Office of Scientific Research and the Materials Science Center.

HIGHLIGHTS

Metals: It has been reported in the literature that crack growth per cycle in fatigue experiments increases rapidly as the temperature is raised. Furthermore, the mode of crack propagation changes from transgranular to intergranular. Also, the rate parameters such as frequency of cycling, holdtime, temperature, as well as the microstructural parameters such as grain boundary precipitates, grain size, and impurities, become important. We have been able to explain these results on the basis that the crack propagation rate is enhanced because the material becomes damaged. The damage is in the form of cavities in the grain boundaries. The primary crack interacts with these cavities which results in a more rapid rate of crack propagation. We have developed (i) the criterion for the initiation of grain boundary cavities and (ii) the criterion for the interaction of the primary crack with these cavities. The results from this work, for the first time, provide a quantitative mechanistic basis for fracture in creep-fatigue. Experiments are being developed to measure crack growth rate in 316 stainless-steels in high temperature low-cycle fatigue.

Ceramics: The objective is to study fracture in ceramics such as hot-pressed silicon-nitride from a microstructural viewpoint. The typical microstructure consists of a fine grained material (grain size - 0.5 to 10μm) and a second phase with a volume fraction of 1→10% which is distributed in the grain boundaries. The second phase is believed to be a glass. In silicon-nitride its glass transition temperature ranges from 800 to 1200°C depending upon the level of alkaline impurities. Initiation of grain boundary cracks is the key to the time dependent fracture in these materials. We have theorized that the rate of initiation of grain boundary cracks is related to the rate of grain boundary sliding which produces stress concentration at grain-boundary triple junctions and the rate of relaxation of this stress-concentration by diffusion and by the redistribution of the grain boundary phase. The rate of sliding which produces stress-concentration and the rate of relaxation of this stress-concentration is related to the thickness and the viscosity of the intergranular phase, to the diffusivity of the principal phase through the intergranular phase, and to the grain size and the elastic constants of the grains. We are developing experiments to measure the viscosity of the intergranular phase using the internal friction technique, and also experiments to measure crack growth in hot-pressed silicon-nitride in tension-compression loading.

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Ultrapressure Materials Science

A. Pressure Generation and Containment

The concept of attaining high pressures by operating in the plastic range was proven; pressures in excess of 85 kbars (InAs transition) have been reached in a steel pressure vessel whose yield strength is 20 kbars (NASA).

We are currently working with two high pressure systems. Our sphere system (NASA) is being used in experiments to obtain the BP transition, predicted at 400 kbars by Van Vecten. It should be noted here that all of his predictions for transition from zincblende to β-Sn structures have been equal to or higher than the experimental values which are available now for 11 compounds; in some cases the product phase is the NaCl structure rather than the β-Sn structure. Thus we would expect that when we reach this transition, we could have pressures of 400 kbars; the transition has not been reached in the U.S. and other reports of it are unconvincing. We hope to obtain it this summer. We are preparing also to attempt to obtain transitions in SiC and A&N which he predicted to transform at 640 and 900 kbars. We are also working with diamond anvils; these have the advantage of being useable for x-ray and optical and spectroscopic research; however these applications are probably limited by the yielding of the diamonds which usually leads to failure as well (which we will discuss later).

We have carried out a detailed analysis of indentors (since these have been used to obtain high pressures) of fairly general shape and have solved the elastic problem of the pressure profile, and the induced shear stress and tensile stresses. We are therefore now capable of designing the profile in such a way as to get the maximum pressure prior to failure assuming the fracture stress and the yield stress are known (which we will discuss later).

B. Pressure Measurement

Pressure (very high) has few physical laws of broad validity such as exist for temperature and provide a means of measuring it (black body radiation for example). There is of course the free piston gauge based on F/A which has been used with liquid systems to 45 kbars and solid systems to 73 kbars. We are working now on a variation of this which could work to 0.5 Mbars (or to whatever is the elastic limit for diamonds). This would be a measure breakthrough in high pressure measurement. At present such pressures are 'measured' by using the shift of the ruby R_1 fluorescence (assumed to vary linearly with pressure) which in turn is calibrated against the NaCl scale. The NaCl scale is used as a primary scale (which it most certainly is not) by assuming that the pressure-volume relation of Born-Mayer (a central force solid) is applicable to NaCl. It has recently been shown by Chhabildas and Ruoff (NASA Contract) that the NaCl scale seriously overestimates the pressure. This implies in turn that the pressure versus ruby shift is a quadratic relation and that the linear ruby scale seriously overestimates the pressure in the

neighborhood of 0.5 mbar. The theory of the ruby shift deserves serious theoretical attention.

We are investigating the possibility of extending the Lincoln-Ruoff absolute pressure gauge. At present, this is the only absolute system except for the free piston gauge.

We are beginning work on the aluminum pressure scale, which we believe can be placed on a sounder theoretical basis than the NaCl scale. This involves lattice parameter measurements in a diamond cell and is hence a quasi-primary gauge. We are continuing work on the ^{7}Be gauge. We are also carrying out work on a resistance gauge which looks thus far quite promising. These latter two are, of course, secondary gauges.

C. Yield Stress

We have developed this year a second method of quantitatively measuring the yield strength of ultrahard materials. This method gave the same results for cemented tungsten carbide as did our first technique announced last year. We currently are applying these techniques to measure the yield strengths of $A\ell_2O_3$, B_4C, TiB_2, Ge, Si, diamond and other hard and brittle materials as well. We expect to have a thorough knowledge of the yield strength of materials ordinarily used in ultrapressure research. Thus if the yield stress of diamond were known we could predict with considerable confidence the maximum pressure available in a diamond cell without yielding on the basis of exact analysis carried out by us this past year. The yield strengths of the ultrahard materials are, of course, of considerable scientific interest as they approach the theoretical yield strength. After the actual yield strengths are measured, we intend to study the mechanisms of the yield process.

This particular work began with NASA support but will be carried out primarily with MSC support.

We also feel that it is distinctly possible that the new techniques which we are developing will have applicability not only to ultrahard materials but to a wide variety of common structural materials.

This research will make two (and possibly four) major contributions:

1) It will provide a method for obtaining the yield stress of ultrahard materials.

2) It will provide the first set of yield strengths of ultrahard materials.

3) It could provide an insight (and possibly a detailed knowledge) into the mechanism of yielding of the ultrahard materials.

4) It could provide a general new method of measuring yield strengths which could be of considerable practical and industrial importance.

D. Synthesis of Metallic Polymorphs

One of our primary purposes in working to generate high pressures is the resultant possibility of creating new metallic polymorphs. In particular we hope to reach sufficient pressures to create metallic hydrogen. These are however, a number of other interesting possibilities including metallic methane and metallic ammonium. Several 3B-5B compounds InSb, GaSb, AℓSb; InAs, GaAs and InP, GaP become metallic at pressures below 220 kbars; as do also the group IV elements Ge and Si, Sn. There is a well established trend among the 3B-5B compounds: (1) As the atomic # of the valence 3 element (in combination with a given valence 5 element) decreases, the transformation pressure increases. (2) As the atomic # of the valence 5 element (in combination with a given valence 3 element) decreases, the transformation pressure increases. Thus the nitrogen compounds should have the highest transition pressure (theoretically estimated to be at 2.1 Mbars). In this same context, the transformation pressure in the group IVB elements increases as the atomic number decreases, Sn being a metal at zero pressure, Si at 120 kbars and graphite predicted to become metallic at 1.7 Mbars. SiC is predicted to become metallic at 640 kbars.

At the present time we are studying BP which Van Vecten predicts will become metallic at

400 kbars. Should we obtain this transition we will next study SiC and then GaN (prediction is 900 kbars). It is our hope to obtain these transitions this year; this would represent a major step toward generating ultra-high pressures. This work is closely related to the subject of pressure measurement inasmuch as these transformation points can serve as calibration points. These of course are secondary points but can be used as quasi-primary points by placing trust in theoretical predictions (the same sort of desperation involved with use of the ^{7}Be and NaCl gauges as primary gauges). It is felt that if BP transforms at 400 kbars, we should be able to reach this point with our new absolute measurement system.

E. Equation of State

We have developed and used sophisticated apparatus for studying the length change of specimen versus pressure. This has been applied to silicon, LiF and now NaCl. The results on LiF and NaCl have been analyzed and accepted for publication. The results on NaCl illustrate the power of this method, inasmuch as we were able to obtain good values of the second derivative of the bulk modulus (by making measurements to 7.5 mbars on a material whose bulk modulus at zero pressure, B_0, is 238 kbars. Similar measurements on a material with a smaller B_0 would lead to a new level of accuracy in determining equation of state. As an example B_0 for potassium is 30 kbars and were our system modified to reach pressures of 30 kbars (and we can do this given support) we could measure both B^S and B^T as a function of pressure or volume and obtain a highly accurate equation of state for a model material to a pressure of B_0 (the equivalent pressure for iron would be 1.6 Mbars). A most important outcome of these results is that the Gruneisen parameter could also be measured accurately as a function of volume. The Gruneisen parameter plays a vital role in transforming shock Hugoniot data into isothermal data. At the present time it is actually known only to a pressure of $B_0/10$. Beyond this, assumptions are made which have little basis in science. It would be most useful to have data on B_0 for a number of materials

F. Fine Particle Materials

Our purpose here is to eventually produce ultrafine particle polycrystalline aggregates beginning with ultrafine particles (initially of one phase but later with more than one phase) by use of hot isostatic compaction. Eventually, we intend to produce grain sizes down to the range where crystallinity merges with the glass state. Our initial interest is to increase the fracture stress of materials such as tantalum carbide and tungsten carbide so that the tensile fracture stress exceeds the tensile yield stress. While we are primarily concerned here with the science of hot isostatic compaction and hence deal with small samples, we mention in passing that we can achieve pressures at room temperature approaching 80 kbars in a cube with 7.5cm edge. We could probably attain pressures of nearly the same magnitude at 1200°C in a cube of 3cm edge, so that the matter of hot isostatic compaction at very high pressures is a real technical possibility. At the present time we have nearly found the optimum conditions for hot isostatic compaction of TaC which yields essentially fully dense solid without grain growth. The properties of these materials are being studied and their microstructure is being characterized.

Research supported by the Materials Science Center.

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The Propagation and Scattering of Ultrasonic Waves in Materials

1. Characterization of Materials

A modified echo-overlap technique was developed and was used to make velocity dispersion measurements of r.f. bursts in multi-filamentary NbTi superconductor composite wires. The measurements using extensional waves show that in these composite wires pronounced dispersion effects are present which differ somewhat from the dispersion effects measured in solid wires. We have concluded from these results that the effective Poisson's ratio of the composite materials is less than that of solid wires. For the attenuation measurements in these materials, a pulse-echo technique was used in which the echoes reflected from and transmitted across a buffer-specimen interface are analyzed to determine simultaneously the frequency-dependent reflection coefficient and specimen attenuation.

Research supported by the National Science Foundation and the Materials Science Center.

2. Time Records and Power Spectra of Scattered Ultrasound

Experiments closely paralleling the analytical work of Professor Pao's research group were continued. The orientation dependence of the scattering of broadband ultrasonic pulses by a cylindrical fluid-filled inclusion in an elastic solid is now well understood. We found significant differences between the time records of the back-scattered signals and the signals scattered into an arbitrary receiving direction. However, as in the earlier, backscattering studies, the arrival times of the signals received at an arbitrary receiver location are in agreement with those predicted by the theory of geometric acoustics.

We have also shown that the pronounced maxima and minima in the experimentally observed spectra of the forward-scattered and back-scattered signals respectively, coincide with the overtone frequencies of the two lowest normal modes of vibration of the cylindrical inclusion. For the 90° side-scattering situation, we have observed that the minima of the spectra coincide with the overtones of the n=0 normal mode of the inclusion. The significance of these results is that the wave speed to radius ratio of the cylindrical inclusion can be determined unambiguously from the ultrasonic spectra in a non-destructive testing application.

Experiments of the scattering by a fluid-filled elliptical inclusion in an elastic solid have begun. The theory of geometric acoustics has been extended to permit the calculation of the arrival times of the signals back-scattered by such an inclusion of arbitrary eccentricity. It is found that when the eccentricity of the scatterer becomes large (resembling a smooth crack), the creep-fluid ray ("halo" ray) observed in the cylindrical scattering situation becomes equivalent to the creep ray which propagates around the shadow side of the scatterer.

Experiments and ray analyses calculations have been extended to the fluid-filled bi-inclusion in an elastic solid. Techniques have been developed which permit the quantitative determination of the size and location of such clusters in materials.

From a series of experiments we have shown the existence of a reciprocity phenomenon in the scattering of elastic waves by obstacles of arbitrary shape. The experimental work was stimulated by the analytical work of Dr. V. S. Varatharajulu. The usefulness of the reciprocity phenomenon is that the number of measurements needed to characterize a scatterer completely are significantly reduced.

Professor Y. H. Pao is Professor and Chairman of the Department of Theoretical and Applied

Mechanics. He is also a member of the Materials Science Center. Dr. V. S. Varatharajulu is a MSC-supported post-doctoral research associate in the Department of Theoretical and Applied Mechanics.

Research supported by the National Science Foundation and the Materials Science Center.

3. Experimental Stress Analysis Using Ultrasonic Pulse Spectroscopy Measurements

A technique was developed which utilizes pulse spectroscopy measurements to analyze the interference effects between the two shear waves propagating in a stress-induced birefringent metal specimen. The frequency of destructive interference between the two shear waves is shown to be related to the difference in principal stresses in a plane-stressed specimen. The sensitivity of the technique in measuring changes in the principal stress differences appears to be higher than obtainable with direct velocity measuring techniques. Experiments investigating the phenomenon in uniaxially-stressed specimens of 6061-T6 aluminum, α-brass, OHFC copper and 304 stainless steel were completed. Experiments utilizing transversely-loaded specimens and diametrically loaded disk specimens are presently underway.

Research supported by the Materials Science Center

4. Non-Destructive Testing of Friction-Welded Materials

In collaboration with Professor K. K. Wang and his student Mr. J. Driscoll, we have shown that the reflection coefficient of ultrasonic waves at the weld region is related to the fracture strength of the welded specimen in an impact test. The results also indicate that the ultrasonic measurements contain information about the interface microstructure and weld area. Current experiments in which the frequency content of the interface signal is determined are expected to delineate between these two effects.

Professor K. K. Wang is in the Department of Mechanical and Aerospace Engineering.

Research supported by Eastman Kodak.

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SURFACE SCIENCE STUDY GROUP

The broad theme which underlies the research program of the Surface Science group is the quantitative study of relationships between atomic and electronic structure of surfaces on the one hand and the chemical and physical properties of clusters on the other, with an increasing emphasis upon the factors controlling chemical reactivity and reaction mechanisms at surfaces. This is carried out through experimental and theoretical projects in the following related areas.

1. Applied theoretical work focussed on the structure and reactivity of organic molecules modified to centers composed of transition metal atoms.

2. Detailed comparative analysis of clusters and surfaces in terms of atomic structure, bond energies, mobility of ligands or chemisorbed species, and of catalytic reactions.

3. Microscopic factors associated with chemical bonding of atoms and of molecules at solid surfaces in terms of their specific electronic and atomic structures, and the role of these factors in the dynamics of reactions localized at surfaces or on small particles.

4. Study of the thermodynamic and kinetic parameters associated with the structure of solid surfaces and the criteria defining physical and chemical transformations particular to two-dimensional systems.

5. Extension and development of ion and electron probes to evaluate the compositional and structural properties characteristic of surfaces and the surface region of diverse systems at new levels of sensitivity and precision.

Surface Science Study Group Membership

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Segregation at Metal Surfaces: Activity of Carbon Covered Transition Metals

A study of the interaction of segregated and adsorbed atoms with free surfaces. The emphasis of this work is on the structure and thermodynamic properties of surface phases, and the understanding of these properties in terms of interactions among adsorbed species and between adsorbed species and substrate. One objective of the work is to develop a general scheme for the description of equilibrium segregation to interfaces in alloys. Considerable effort is directed at studying the influence of surface defects such as steps and kinks on the binding of adsorbed and segregated atoms. The systems being studied are dilute alloys of carbon in Ni and Pt. The reversible segregation of carbon to various single crystal surfaces of the alloys is being studied using LEED, secondary electron spectroscopy and other surface science techniques. The equilibrium of quasi-2-dimensional surface phases is being studied in detail on both planar and stepped single crystal surfaces. Modulated molecular beam studies of the catalytic efficiency of surfaces with various carbon overlayers for simple hydrocarbon reactions are in progress.

Research supported by the National Science Foundation and the Materials Science Center.

Oxidation of Metal Surfaces

A study by electron spectroscopy and diffraction of the initial stages of oxidation at well characterized single crystal surfaces. The properties being investigated are the kinetics of growth, the structure of the oxide film and the transition in electronic structure from that characteristic of the clean metal to that of the oxide. Experiments in progress deal with the formation of oxides on single crystal planes of the divalent metals including Be, Mg and Zn. Both the pure metals and the bulk oxides of these elements have been studied in some detail and they are attractive materials from an experimental viewpoint. The emphasis of the work is on the formation of the first few monolayers of oxide.

Research supported by the National Science Foundation and the Materials Science Center.

Surface Properties of Silver and Silver Halides

Part of this program is concerned with the distribution of point defects and space charge layers at and near free surfaces of ionic crystals and metal-ionic crystal interfaces. In the silver halides, used as photographic materials, these layers are of special interest due to their role in latent image formation. The segregation of divalent sensitizing, doping elements such as Cd to free surfaces is being studied to try to understand the role of these dopants in surface latent image formation. The interaction of halogens with silver surfaces is of interest to both in understanding the photographic process and in connection with the use of silver catalysts for oxidation reactions. Silver is used as a catalyst for the oxidation of ethylene and the reaction.

is known to be moderated by small surface concentrations of C . We are currently studying the adsorption of chlorine on various singular and vicinal surfaces of silver crystals in an effort to identify the types of sites at which Cℓ is most strongly bound. We intend to study the co-adsorption of $C\ell_2$ and O_2 on silver and also carry out experiments on C_2H_4 oxidation using the modulated molecular beam technique.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

In the study of segregation of carbon to single crystal nickel surfaces we have obtained sets of segregation isosteres from which model independent heats of segregation may be derived. These have also been used to provide tests of the validity of Langmuir adsorption equations in describing the segregation behavior. The effect of steps on the magnitude of the binding of carbon to nickel surfaces has been investigated. Steps on surfaces near (100) enhance the binding of carbon atoms; other surfaces are currently being studied.

A detailed study has been made of the Auger line shapes and electron energy loss spectra during the formation of ZnO on the basal plane of Zn single crystals. The low energy Zn Auger peaks shift and change shape during oxidation in such a way that intermediate states can be represented as linear superpositions of spectra from the final oxidized and initial clean surfaces. This suggests that the oxide grows heterogeneously on the surface. The Auger spectra from epitaxial ZnO and from clean Zn (0001) can be understood quite well on the basis of current information on the bulk band structures of those materials; the energy loss spectra are in reasonably good agreement with data on optical reflectivity.

The adsorption of $C\ell_2$ on the (110) surface of silver has been shown to be reversible with pressure cycling above ~400°C and both isotherms and isosteres have been obtained for this surface. The heat of adsorption is in the region of 2eV per molecule of $C\ell_2$ and analysis of the isotherms at 458, 477, and 560°C shows that they can be rather well represented by the Langmuir theory. Details of the Auger spectra and structural transformations, indicated by LEED, will be studied on this and other silver surfaces.

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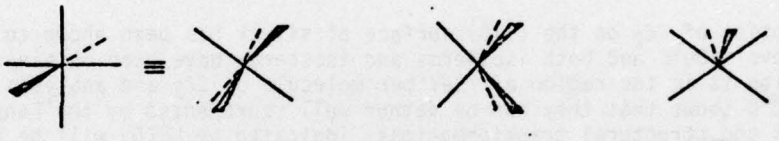
Electronic Structure of Transition Metal Complexes

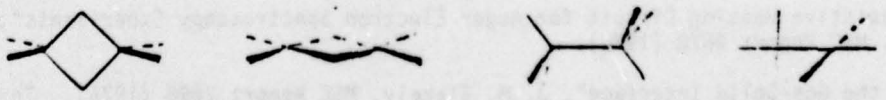
(A) We examined theoretically the trigonal prism, 2, and the bicapped tetrahedron, 3, as alternatives to the common octahedron, 1, for six-coordinate main and transition group compounds. The pronounced preference of six-coordinate sulfur for an octahedral geometry is traced by a molecular orbital analysis to a pair of non-bonding levels, whose higher energy in the non-octahedral



1 2 3

geometries is due to the molecular orbital equivalent of a ligand-ligand repulsion. For transition element complexes we draw a correlation diagram for the trigonal twist interrelating octahedral and trigonal prismatic extremes. A possible preference for the trigonal prism in systems with few d electrons is discussed, as well as a strategy for lowering the energy of the trigonal prism by symmetry-conditioned π bonding. The bicapped tetrahedron geometry for transition metal complexes can be stabilized by a substitution pattern ML_4D_2 where D is a good σ donor, M a d^6 metal center.

(B) Continuing a study of metal-metal interactions which previously focused on weak interactions (J. Amer. Chem. Soc., 97, 4884 (1975)), we have now looked at coupling of medium strength. More specifically, we have completed an analysis of M_2L_6 dimers. These can assume a range of geometries specified by the extreme structural types of a tetrahedral dimer, 4, square-planar dimer, 5, the ethane-like geometry, 6, and the metal-metal bonded 7. Variations bridging these geometrical extremes exist as well. Three factors influence the geometry and electronic structure



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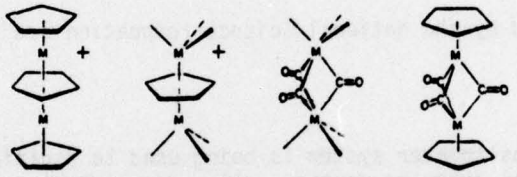
of dimeric tetrahedral and square planar transition metal complexes of the M_2L_6 type. The factors are 1. The geometrical preference of the monomer, 2. the symmetry-restricted opportunities for coupling through the orbitals of the bridging groups, 3. direct metal-metal overlap. In analyzing the first factor, we find that in tetrahedral d^{10} monomers of the MX_2Y_2 type the angle between the better π acceptors and better σ donors should be opened up. The structures of monomeric dinitrosyls are rationalized, including the minor deviations from NMO linearity. Superposition of the calculated MX_2Y_2 monomer structures into a $X_2MY_2MX_2$dimer gives a reference point relative to which elongation or contraction of the bridge region as a consequence of through-bond coupling or metal-metal bonding can be evaluated. In the tetrahedral d^9 dimers we find little direct metal-metal σ bonding, in the d^8 dimers a strong metal-metal π bond. Locally square dimers are studied, with an emphasis on the interconversion of the alternate square planar and tetrahedral geometries. The orbitals of the bridging group are determinative here, with π-donors favoring the square planar extreme. The simple twist interconverting the two structures is symmetry forbidden. We study the hinging distortion in the square planar dimer, failing to find a controlling electronic effect for this soft surface.

(C) By making use of the frontier orbitals of metal-cyclopentadienyl (MCp) and $M(CO)_3$ fragments, the electronic structure of triple-decker sandwiches CpMCpMCp, 8, and $(CO)_3MCpM(CO)_3$, 9, was analyzed. Two series of stable structures, containing 30 and 34 valence electrons respectively, are predicted. The known $Ni_2Cp_3^+$ and $Co_2Cp_2(C_2B_3H_4R)$ triple-deckers are representatives of these two series. There are important similarities between these compounds and normal triply CO bridged dimers of the $Fe_2(CO)_9$, 10 type. The theoretical analysis is extended to types such as $(CH)_nM(CO)_3M(CH)_n$, 11, suggesting a number of potential synthetic goals.



8 9 10 11

Research supported by the National Science Foundation and the Materials Science Center.

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Research in Ion Microscopy of Solid Surfaces

During this past year a new research program was started involving ion microscopy and ion microprobe analysis. Emphasis was placed on both the fundamental aspects of the technique to improve quantitation, and its application to the study of metals, alloys, semiconductors, and devices.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

A computerized densitometer system is being used to digitize ion micrographs for quantitative measurements. Present software routines allow reorientation of images, contour plotting, and fast Fourier transform for filtering and cross correlation between similar images.

An investigation is in progress directed toward an understanding of the processes surrounding ion bombardment, including sputtering and ionization, with major emphasis on developing a good theoretical model allowing quantitative analysis. A computational equation involving a single fitting parameter has been developed for quantitation of ion intensities.

The largest source of error in microprobe analysis is due to the sampling of heterogeneous materials. Mathematical formulas have been designed to estimate the expected sampling error as a function of the degree of heterogeneity. Good correlation has been found between calculated and experimentally determined error.

The application of secondary ion mass spectrometry to the study of thin (angstroms) and thick (microns) oxide films is being investigated. Using an oxygen leak system, SIMS was employed for in situ controlled growth and analysis on freshly cleaned surfaces. The study is being applied to semiconductor materials and metals.

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Synthesis of Organometallic Compounds and Evaluation of Their Catalytic Activity — US-USSR Program of Scientific and Technical Cooperation in the Field of Catalysis

A research associate, a magnetic resonance spectroscopist, from the Institute of Chemical Physics in Moscow is working in our laboratories for a period of six months. His research objective is a spectroscopic study of exchange phenomena in metal clusters and an analysis of the significance of these intramolecular and intermolecular exchange processes to the catalytic activities of the metal clusters. Two research associates from our group, J. Atwood and W. Pretzer have spent six month periods in Moscow at the Institute for Chemical Physics on mechanistic studies relating to the general subject of nitrogen fixation.

Research supported by the National Science Foundation and the U.S.S.R. Academy of Sciences.

Synthesis of Coordination Compounds — Design of Homogeneous Catalysis

New types of catalytic reactions are sought through the design of new classes of coordination and organometallic structures with optimal electronic, stereochemical and functional group features for the interaction with and subsequent activation of important small molecules like H_2, N_2, RCN, CO and hydrocarbons. Structural and reaction mechanism studies comprise a key part of this program since a fundamental understanding of the chemistry is essential to a logical development of new catalytic chemistry. A major element in the research is the development of the catalytic chemistry of discrete metal clusters. This area is viewed as a possible bridge between homogeneous and heterogeneous catalysis. Other major research efforts include (1) a mechanistic study of the olefin metathesis reaction, (2) catalytic hydrogenation of aromatic hydrocarbons, (3) development of low valent metal phosphite chemistry and (4) basic studies of metal hydrides, metal alkyl complexes, and metal alkyls in catalytic, or related, reactions.

Research supported by the National Science Foundation, the Advanced Research Projects Agency and the Materials Science Center.

HIGHLIGHTS

A new class of tetrahedral nickel clusters has been prepared and structurally defined. The parent member is Ni_4L_7, with L an alkyl isonitrile, ligands unsymmetrically bridge tetrahedral edges in a common face. In $Ni_4L_4(RC{\equiv}CR)_3$, the diphenylacetylene ligands bridge edges in a symmetrical fashion. Other molecules with triple bonds, e.g., nitriles and aryldiazonium cations, can bridge in an analogous fashion. These triply bonded molecules interact with the metal atoms so as to substantially reduce the bond as evidenced by bond length and by chemical reactivity. These clusters present an effective means for the activation of triple bonds towards reduction in key molecules like CO, N_2, acetylenes, nitriles, isonitriles and cyanide ion. Catalytic hydrogenations of acetylenes (selectively to cis olefins), nitriles, and isonitriles (stoichiometric) have been demonstrated with these nickel clusters and the hydrogenation of CO to CH_4 was achieved with iridium and osmium carbonyl clusters. The mechanisms of these catalytic reactions are now under study in attempts to develop mechanistic comparisons between the catalytic chemistries of metal clusters and metal surfaces.

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Chemosorption and Catalysis

The major area of research has focussed on the interaction of electrons and atoms with metal surfaces in order to understand in more detail the mechanism of these interactions from an atomistic and electronic viewpoint. The principles and features of chemical bonding at surfaces are then related to aspects of heterogeneous catalysis. The main emphasis of study continues to be the mechanisms of simple chemical reactions involving molecular reactions of oxides of carbon and of nitrogen with hydrogen or oxygen as well as hydrogenation, dehydrogenation, cyclization and fragmentation of simple hydrocarbons such as olefins and substituted aromatics. Surfaces of plantinum group metals; particularly platinum, iridium, palladium and rhodium are of particular interest. Their geometric, microscopic and compositional properties are characterized using various ultra high vacuum surface probes in combination including photoelectron spectroscopy, LEED, Auger spectroscopy, thermal desorption and electron tunneling spectroscopy. In this work, synchrotron radiation using the electron storage ring facility at Stoughton, Wisconsin is playing an increasingly important role. Exploring the mechanism of surface reactions by this method is facilitated by the intense collimation of the beam, its variable frequency and the unique feature of its planar polarization.

Research supported by the National Science Foundation and the Materials Science Center.

Electron Properties of Corrosion-Resistant Metals

The detailed nature of the interaction of reactive molecular gases with corrosion-resistant metals and alloys, primarily those based on iron, chromium and nickel is being investigated. Emphasis is placed on measuring the physics of electron interactions in these materials with the objective of developing new principles defining their unique capability to develop resistance to normally strongly corrosive environments. Although the surface probes used here are similiar to those described above, this work is focussed strongly on defining the mechanisms involved in terms of new and detailed information on the electron nature of alloying, chemical bonding and resistance to chemical degradation in these materials.

Research supported by the American Iron and Steel Institute and the Materials Science Center.

HIGHLIGHTS

The polarization properties of photoelectron excitation were used for the first time to investigate the orbital symmetries and geometric orientation of the chemisorbed CO-molecule on the Ir(100) surface. The significance of this work is that it illustrates how hitherto inaccessible information on the details of chemical bonding at surfaces can be obtained by analysis of photo-electron emission using a synchrotron radiation facility.

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OPTICAL PHENOMENA STUDY GROUP

The broad membership of this Study Group reflects the widespread scientific and technological interest in the many interactions of laser light with condensed matter. Among the primary objectives of this group are: i) the development of new laser based optical techniques to study the structure of solid state materials, ii) to develop a better understanding of the various processes whereby laser radiation interacts with condensed matter, and iii) in carefully selected instances, to apply the information obtained to the development of new and improved optical materials and devices.

The research programs of a significant fraction of this Group focus on the shared use of one of the newer MSC central facilities, the Dye Laser Facility. The group has been particularly successful in developing a communal Facility with unique capabilities and in integrating the research programs of its members with this Facility. All members participate extensively in the planning and operation of this Facility, with bi-weekly seminars and strong interactions between technique-oriented and problem-oriented members.

The Dye Laser Facility is now in its fourth year of operation, and has grown rapidly in size and level of activity as members have increasingly focussed their programs on the Facility's special capabilities. It now fills three rooms with two large cw argon ion pump lasers and a pulsed nitrogen pump laser and six tunable dye lasers with different characteristics. There are usually about eight active experiments underway which utilize these tunable sources. Most of the signal detection and processing equipment and spectroscopic apparatus in the Facility has been provided by the participating members. The Facility is unique not only for its size and scope, but also for several capabilities available nowhere else, among them fast electronic dye laser tuning and injection-locked picosecond lasers.

Optical Phenomena Study Group Membership

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Electronic and Vibronic Spectroscopy

This program is designed to study the effects of nuclear motion on the electronic properties of organic molecules, including transition moments, radiative and radiationless relaxation processes and Raman intensities. The experimental techniques include the use of polarized photoselection analysis in rigid glasses, polarized crystal spectroscopy, Stark effect studies, phase shift analysis of relaxation processes, electroluminescence, etc. A new ultra sensitive thermo-optical spectroscopy is being explored for detecting very weak transitions such as overtone transitions and spin-forbidden transitions. The results are tested against variation-perturbation analysis of model systems.

Research supported by the National Science Foundation, the Advanced Research Projects Agency and the Materials Science Center.

Electronic Spectroscopy and Two-Photon Absorption

This program utilizes two-photon absorption processes via real states to probe the electronic states of organic molecules. CW and mode-locked lasers are used to pump short-lived singlet states and intense secondary beams are used as spectroscopic sources. Photoionization from excited singlet states is explored. Sub-nanosecond lifetimes are measured for recombination luminescence in organic systems. The thermo-optical spectroscopy used in the pulsed mode appears to offer a new, sensitive tool for studying two-photon spectroscopy in the liquid state.

This project and the above, entitled "Electronic and Vibronic Spectroscopy" are basic studies directed towards the understanding of the electronic structure of large polyatomic molecules and how this structure is sensitive to nuclear position. Such studies are vital to the testing of various theoretical methods for treating molecular structure and have the deeper aim of understanding the short-lived molecular states which control rates of chemical change.

Research supported by the National Science Foundation, the Advanced Research Projects Agency and the Materials Science Center.

Photoelectric and Photochemical Properties of Rigid Organic and Ordered Organic Solids

This program is concerned with electron states in amorphous organic solids and solutions,

and suspensions of organic crystallites. Solvated or trapped electrons are investigated with photoconductometric, spectrophotometric and electron spin resonance techniques. Electrophotoluminescence also provides a measure of the recombination of matrix trapped electrons with correlated positive centers. Photoelectric and photovoltaic effects due to junction barriers at metal-organic solid or solution-organic solid interfaces are being explored.

The deeper aims of the projects relate to the role of electron generation and transport in biological systems — in particular in photosynthesis. Also the organic analogue of inorganic semiconducting devices is being explored.

Research supported by the National Institute of Health, the Advanced Research Projects Agency and the Materials Science Center.

HIGHLIGHTS

I. Electronic and Vibronic Spectroscopy

R. Swofford has been helping M. Burberry and J. Morrell establish themselves with the thermo-optical spectroscopic technique. Work has been completed on the overtone spectroscopy in the visible region of aromatic hydrocarbons, and the O-H group in alcohols. The apparatus has been interfaced with a Digital Processing Oscilloscope and a PDP 11 computer for data processing and control. Th· double-beam spectrometer has been perfected permitting automatic scanning.

M. Burberry has been active in solving the quantum mechanics of the anharmonic oscillator — particularly with the view of obtaining overtone intensities.

G. Korenowski has developed a program package for handling all varieties of resonance Raman situations as predicted by our theory for resonance and preresonance Raman intensity. He also continues preparing for measuring Raman scattering from excited electronic states.

A. Kriebel has completed a theoretical study of a trimer excitonic model for bacteriorhodopsin bound to the membrane. He has carefully characterized our comparative phase fluorimeter using both conventional and CW laser illumination. Under ideal conditions laser excitation seems to promise 10-15 p sec resolution while conventional light sources offer less confidence at this level.

J. Morrell is beginning an experimental effort in electro-thermo-optical spectroscopy. This new, untried, technique should be able to measure dipole moments of chemical bonds. He also continues his theoretical activities aimed at calculating equilibrium geometries and force fields of excited electronic states.

L. Ziegler has made excellent progress in using tunable ultraviolet laser radiation. He is doubling N_2 laser pumped dye lasers for this purpose. He already has obtained preliminary near resonance Raman data in the quartz ultraviolet. He has not yet tried site selection spectroscopy.

C. Merlo is just beginning her work. She is considering a project which will attempt to see singlet-triplet (spin-forbidden) transitions in a variety of molecules of photochemical importance. Their triplet states have never before been directly located. Thermo-optical spectroscopy should provide the means for first locating these states spectroscopically.

C. Hemenway is just beginning to attempt near picosecond fluorescence lifetime measurements using the up-conversion technique developed by Mahr's group. His first molecule for study will be crystalline Chlorophyll-a.

II. Electronic Spectroscopy and Two-Photon Absorption

L. Ziegler has verified D. Kliger's (Santa Cruz) observation that thermo-optical spectroscopy using a N_2 pumped dye laser forms a very powerful tool for seeing two-photon (virtual state)

absorption in liquids. He obtained a very nice such spectrum in benzene. In principle all liquids should reveal such behavior in the ultraviolet.

J. Gilberg is beginning to explore biphotonic ionizations using N_2 pumped dyes (doubled).

III. Photoelectric and Photochemical Properties of Rigid Organic and Ordered Organic Solids

C. Conley continues his difficult, as yet unsuccessful search for magnetic perturbations of electron-cation recombination in rigid organic solutions. A major effort this year has been to develop equipment capable of temperatures near 2°K. Studies at this temperature will be attempted momentarily. Recombination luminescence kinetic data (with no magnetic field) have been obtained at 4°K.

A. Doheny is completing his work on electric field perturbation of recombination luminescence. He has worked out the electron tunneling model predictions at a variety of fields and including the Coulomb field of the cation. He has changed media to one which is harder at 77°K than that previously used. Pure tunneling kinetics are now observed, unlike before.

T. Imura is visiting from Japan. He carried out some exploratory flash photoconductivity studies of bacteriorhodopsin in ice. He is also interested in phase fluorimetric lifetime studies of chlorophyll in various absorbed states.

T. Yamamoto is busy exploring the photovoltaic behavior of Chl-a films interfaced with aqueous solutions. She hopes to test whether Chl-a is able to bring about the photocatalyzed electrolysis of H_2O.

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Active Electromagnetic Effects in Semiconductors

I. Electroluminescent Metal-Insulator-Semiconductor (MIS) Structures

This program involves theoretical and experimental investigations of luminescent MIS structures and has as its ultimate objective the production of efficient room temperature light-emitting or lasing devices which could be compatible with integrated optical systems. Work this year was concentrated on the Pt-Al_2O_3-CdS and Al-Al_2O_3-CdS structures with the objective of seeing if an efficient tunnel injection device emitting in the visible spectral region and at room temperature could be constructed. In agreement with earlier work on GaAs sandwiches it was found that Al was a much better behaved counter electrode than Pt. CdS devices with Al counter electrodes enabled us to procure for the first time the spectrum of these devices both at liquid nitrogen and at room temperatures. These spectra showed a strong band gap component. Structures with a configuration Al-Al_2O_3-CdS exhibited D-C broadband electroluminescence with voltage thresholds less than 2V (Al positive). This threshold shows that there is significant band bending with CdS which enhances tunnel injection of minority carriers, in agreement with the earlier results on GaAs sandwiches. Calibration for absolute efficiency is not yet complete, but preliminary indications are that injection efficiencies and internal quantum efficiencies are near unity. Additional work on absolute efficiency measurements and on the achievement of stimulated emission in these structures is continuing. These devices have the potential of being an efficient source of blue light.

Research supported by the National Science Foundation and the Materials Science Center.

II. Materials and Structures for Active Optical Devices

Work in this area is being carried out in conjunction with Professor Tang and his group. Our part of the program is directed towards the preparation of materials and structures for semiconductor lasers and detectors. A number of structures with which we are concerned utilize periodic structures in the form of corrugated wave guides. In the area of preparation of semiconductor materials, work progressed on the epitaxial growth of GaAs-GaAlAs heterostructures and epitaxial layers by liquid phase and vapor phase epitaxy. Double heterostructure lasers in this system were fabricated with state-of-the-art thresholds, and techniques for holographic grating fabrication, chemical etching of gratings and epitaxial growth over gratings have been perfected. New methods for exposure control of holographic gratings, a new buffered etch for etching gratings into GaAs through photoresist masks, techniques of cleaning corrugated GaAs substrates prior to epi growth, and a method for eliminating wetting problems under the growth conditions (low contact temperatures, large supercooling and fast cooling rate) necessary to preserve corrugated interfaces have all been developed to the point where near 100% yield of initial substrates to final multilayer wafers with corrugated interfaces is achieved. These wafers are being used in a variety of experiments (tunable diode lasers, Q-switched lasers, and optical filter measurements). While techniques for liquid phase epi growth of GaAs and GaAlAs are now developed to a high state of perfection, progress on the vapor phase growth of epi layers in this system has been disappointing. The vapor epi reactor system has still not produced good epi layers. With the addition of a larger Ga source and modified temperature gradients we are hoping to correct this deficiency very soon; since vapor epi may possess some advantages for growing on corrugated substrates.

In the area of corrugated waveguides a theoretical approach developed for grating couplers

was applied to derive the threshold condition of DFB lasers in a very general manner which includes the effects of coupling between the oscillating guided field and radiation modes. The effect of this coupling is to change the dependence of the threshold gain on the amplitude of the periodic perturbation; increasing the depth of the grating beyond an optimum value causes an increase in threshold due to larger coupling to radiation modes. Previous theories did not include the radiating modes and predicted a monotonically decreasing threshold with increased grating depths.

Further calculations on the reflectivity of an imperfect grating filter were carried out using a new approach based on impedance matching waves on either side of each groove boundary in the grating. The method appears to be straight-forward, elegant and quick and in contrast to earlier approaches for treating random deviations has enabled us to correctly reproduce exactly all published curves for effects of chopped periods, thickness variations, varying coupling constant, etc. and gives nice solutions when random fluctuations are introduced. It predicts that grating reflectivity is relatively insensitive to random fluctuations (on the order of 1%). Experiments are in progress to check this result. If true, it means that the SEM will be a very useful tool for producing periodic waveguide structures. Measurements on corrugated GaAs waveguides will be carried out using a tunable nitrogen pumped infrared dye laser which was constructed during the year and operates with peak power about 14 W (10 nsec pulse), linewidth 0.5 to 0.75 Å, and tunes from 830 to 975 nm.

Progress was made towards developing a rapid electronic tuning semiconductor laser. A system was set up and optical monitoring methods developed for antireflection coating semiconductor lasers. These lasers have been used in conjunction with an external cavity and the electro-optic tuner developed by Professor Tang for dye lasers to provide tuning of the semiconductor diode. Preliminary results are quite encouraging; if successful such a laser should have interesting applications in optical communication systems and infrared spectroscopy.

A scanning laser microscope was constructed during the year. The system will be used to evaluate semiconductor epitaxial layers grown for optical devices. It will provide the capability for doing photo luminescence studies of impurity distributions, effects on minority carrier lifetimes due to inhomogeneities and dislocations, and reflection and transmission microscopy with area resolution of about 1 micron. The system was designed and constructed by a team of Master of Engineering students and we expect it to find wide application for evaluation of the epitaxial semiconductor layers we are growing.

Research supported by the National Science Foundation, the Materials Science Center and the College of Engineering.

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Postdoctoral Associates:

E. Bar-Ziv
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A. Devir
J. Haberman
D. Wu

Research Assistants:

D. Frurip

David Frurip

Completed his Ph.D. project on "Studies of Homogeneous Nucleation in Metal Vapors", and was granted a Ph.D. degree at the June commencement. His thesis work consists of three units: (a) Determination of the critical supersaturation ratio as a function of temperature for iron, lead, and bismuth vapors, and comparison of his data with predictions based on published theories. There are evidently discrepancies, particularly for bismuth. (b) Determination of the kinetics of growth of lead clusters by light scattering. These data are well accounted for by a simple kinetic theory model. (c) Extended calculations for a kinetic model for homogeneous nucleation.

He left Cornell at the end of the spring term for a Post Doctorate post at the Argonne National Laboratory.

Research supported by the Materials Science Center.

Dan Wu

Studied the early stages in pyrolysis of methane (in argon), and the initiation mechanism for its oxidation under fuel rich conditions, using shock tube techniques with laser-schlieren diagnostics. He obtained interesting results but most of his effort was spent in investigating spurious effects in the equipment, and developing reliable methods for data reduction.

Research supported by the National Science Foundation.

Ezra Bar-Ziv and J. Haberman

They worked in parallel on closely related problems, the objective being to find combinations of metal bearing compounds such as SiH_4, B_2H_6, $Sn(CH_3)_4$ which when mixed with oxidizers, such as N_2O, O_2, NF_3 would generate non-thermal populations of excited MX* species. This was accomplished by exposure of suitable mixtures (to which SF_6 was added) to a pulse of CO_2 laser radiation (20J in μs). The hope was that among these non-thermal excitations there would be an inverted population which could serve as a basis for a chemical laser in the visible. While very high luminosities were generated and some were demonstrated to have to be due to very high vibrational temperatures in the upper electronic states, no lasing combination was discovered either in the visible or in the infrared. This project is nearing its termination and was not renewed by the sponsoring agency.

Research supported by the Air Force Office of Scientific Research.

Adam Devir

He set up a CARS unit for operation in the red and near infrared based on a pulsed ruby

laser. This proved to be much more difficult than anticipated. However he has now developed techniques for controlling the ruby laser pulse and the associated dye laser. Intended use of this combination is to vibrationally pump methane gas to develop substantial populations in the totally symmetric stretching mode and to measure fluorescence in the infrared from the asymmetric stretch, at various pressures and mixtures. Thus, we hope to obtain values for the inter- and intra-vibrational energy transfer rates.

Research supported by the Air Force Office of Scientific Research.

K-R Chien

Continued with the study of the laser augmented pyrolysis of D_3BPF_3 and obtained very interesting data which led us to a mechanism of the multiphoton absorption by this compound. He demonstrated isotopic selectivity both with respect to the $^{10}B/^{11}B$ and H/D species. He also made numerous measurements of the rates of group displacement reactions among the borane adducts. The first study has appeared in the Journal of Physical Chemistry and the second part of his work has been submitted for publication.

Research supported by the Army Research Office, Durham.

HIGHLIGHTS

Homogeneous Nucleation in Metal Vapors

We have developed a kinetic model for homogeneous nucleation which is free from the inherent ambiguities and difficulties of the classical nucleation theory. This work has been presented at several meetings and has received substantial attention from the experts in this field.

Laser Augmented Reactions

Our studies of laser augmented reactions is the first in such work in which a quantitative analysis of the yields have been accounted for on the basis of a rational theory.

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Research Assistant:

K-K Hui

Experiments Concerning the Laser Enhanced Reaction Between O_3 and NO

Recent studies have demonstrated that laser-induced vibrational excitation of O_3 results in a large enhancement in the reactivity of O_3 with NO by the reactions

$$O_3^{\dagger} + NO \rightarrow NO_2^* (^2B) + O_2 \qquad (1a)$$

$$\rightarrow NO_2^{\dagger} (^2A) + O_2 \qquad (1b)$$

We have examined the enhancement in chemiluminescence from $NO_2^*(^2B)$ and $NO_2^{\dagger}(^2A)$ in response to the excitation of O_3 by laser absorption ($O_3+h\upsilon \rightarrow O_3^{\dagger}$). Our observations permit a determination of the branching ratios for reaction by processes (1a) and (1b). The principal conclusions of these measurements are:

1) The υ_1 and υ_3 modes of O_3 are responsible for the observed enchanced reactivity (it was previously thought that the υ_2 mode was responsible).

2) The enhancement of the rate constant for reaction (1a) leading to electronically excited $NO_2^*(^2B_1)$ is twice as great as the enhancement of reaction (1b) which yields vibrationally excited $NO_2^{\dagger}$ (^2A) molecules.

3) The activation energies of both processes are reduced by approximately 1 Kcal/mole.

A detailed understanding of the role of vibrational excitation in reaction rate enhancement by reactions (1a) and (1b) will be useful in the development of chemical lasers and techniques for isotope separation.

Research supported by the Air Force, the National Aeronautics and Space Administration, the Office of Naval Research and the Materials Science Center.

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Research Raman Scattering in Crystals

The objective of this project is to use laser Raman scattering techniques to investigate elementary excitations in crystals. The current focus is on scattering from various magnetic excitations in antiferromagnetic cobalt perovskites, particular $RbCoF_3$. In the past year it became clear that the controversy over polarization properties of the scattering is largely due to differences in the domain distributions in different samples seen at different wavelengths. The domains have been shown to be quite large, of order 1 mm on a side, in x-ray topography measurements at Grenoble. We also find such domains when we probe the spatial variation of the polarization in the bulk of the sample with a laser beam from the R6G dye laser. The surface domains, seen with a strongly absorbed laser frequency, tend to be different. In any case, the previous assumption that the domains are microscopic and randomly oriented is invalid. Samples can be made monodomain upon application of a small uniaxial stress, and work is progressing to measure the spectra for monodomain samples at different wavelengths.

During the year we also examined the magnetic-field dependence of the Raman features in $RbCoF_3$. Experiments at 45 kG were performed with P. Moch in Paris. The rather puzzling result was that there were no detectable splittings or shifts. This result was also found by J. F. Scott at Colorado for the same sample at higher fields (130 kG).

In another area of activity, we have continued the study of impurity-induced Raman scattering in crystals, looking at the dynamics and resonant scattering behavior of molecular impurities. Preliminary measurements were made on a heavy molecular ion, ReO_4^- in KI, in collaboration with Sievers. Earlier measurements on the S_2 ion in alkali halides and the $O_3^-(?)$ ion in CaF_2 were reported.

Research supported by the National Science Foundation through the Materials Science Center.

Raman Scattering in Polymeric Solids

This project involves the use of Raman scattering techniques to investigate the structure and dynamics of systems of oriented polymers with novel properties. Of particular interest are those which exhibit "quasi-one-dimensional" physics.

One of the systems studied this year was polysulfur nitride, $(SN)_x$, a "metallic" polymer which behaves like a highly anisotropic semi-metal to low temperatures, becoming superconducting at 0.3K. Dr. Temkin has just completed a first successful study of the Raman scattering in crystals of $(SN)_x$. He finds that the Raman scattering in the metallic crystals is surprisingly strong, very anisotropic and better-resolved than in $(SN)_x$ films. The modes observed are intrachain optical vibrations some of which should couple strongly to charge density waves. The Raman spectrum shows an interesting variation for different tunable laser frequencies in the neighborhood of the plasma frequency, $\hbar\omega_p \approx 2.5$eV.

Some preliminary measurements have also been made on films of a class of magnetic polymer, the poly (metal phosphinates). These polymers, provided by Professor Scott, consist of transition metal ions bridged by phosphinate groups. One can choose different magnetic ions and also different

bridging arrangements to achieve different exchange coupling. Scott has shown from low temperatures susceptibility and specific heat measurements that these chains are magnetically ordered but very sensitive to disorder within and between chains. Dr. Temkin has made some preliminary Raman measurements on ordered and disordered films of poly (chromium phosphinates). The spectra are complicated by the presence of many quasi-localized vibrational modes of the bridging groups.

Research supported by the National Science Foundation through the Materials Science Center

Resonance Raman Scattering in Biological Macromolecules

This program, now entirely supported by NIH, involves the use of resonant Raman scattering with tunable dye lasers to investigate the local conformation of heme proteins in solution.

Work in the past year has focussed on two areas:

a) Mr. Collins is now completing his thesis study of resonance Raman scattering in one of the simplest heme proteins, cytochrome c, and its derivatives. Using ion lasers and tunable dye lasers to excite in the region of the visible absorption bands, the Raman scattering from vibrational frequencies have been shown to be sensitive to spin and oxidation state and to ligand and peripheral substituents.

In the work done so far, most of the Raman spectra have been measured for heme proteins in liquid solution at or near room temperature. During the past year, we have succeeded in measuring the first Raman spectra at low temperatures, using solvents which form clear glasses. Since the optical absorption structure is much better resolved at low temperatures, the dispersion is seen, a "dip" in the depolarization ratio at resonance, which seems to reflect an interference between scattering from nearly-degenerate intermediate states. This appears even when the splitting of these states cannot be resolved in absorption. Measurements at temperatures down to 2K also show that the vibrational frequencies are unchanged, indicating that there is no local conformation change to confound EPR, Mössbauer and other low temperature techniques.

b) Dr. Champion and Mr. Remba are making a study of resonant scattering in several heme proteins of current interest where the iron atom is in different charge or spin states, or where different ligands are expected to modify the heme group. The most successful example has been chloro peroxidase, for which spectra at various temperatures and various pH's with various ligands have been obtained.

Research supported by the National Institutes of Health.

HIGHLIGHTS

1. First Raman measurements on crystals of the metallic polymer, $(SN)_x$. The scattering due to intrachain optical phonons is strong, highly polarized, and shows an interesting variation near the plasmon frequency.

2. Observation of antiferromagnetic domains in $RbCoF_3$ by spatial scanning of the laser beam to detect Raman polarization changes.

3. Discovery of a new resonance phenomenon in Raman scattering, a sharp "dip" in the depolarization ratio, which appears to be due to interference between nearly-degenerate intermediate states.

4. First resonance Raman spectra of heme proteins at low temperatures, using clear glassy solvents. The resonance effects are much more pronounced at low temperatures.

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Energy Transfer and Vibrational Deactivation in Molecule-Molecule and Molecule-Atom Collisions

To provide data for modelling and optimization of chemical and molecular lasers, studies are being made of the rates at which energy is exchanged or redistributed upon collisions of excited molecules with other molecules and with atoms.

Laser induced fluorescence techniques are being used for quenching studies of CO and CO_2 excited molecules. Additional temperature dependence data has been obtained for O atom quenching of CO(v=1) molecules. The new class of lasers employing E→V energy transfer from $^2P_{\frac{1}{2}}$ halogen atoms to CO and CO_2 can be excited using a variety of excited atom sources - i.e. Br_2, CF_3Br etc. and measurements are in progress to determine the quenching rates of CO and CO_2 molecules by a variety of these sources.

Research supported by the Advanced Research Projects Agency and the Materials Science Center.

Laser Induced Photochemistry and Kinetics

A short pulse tunable visible dye laser is being used to excite specific molecular electronic levels and study subsequent quenching or photodecomposition processes. Specific quenchers of importance in a variety of iodine atom lasers are being examined to provide rate constant data for kinetic modelling. Effects of isotope substitution are being studied in order to elucidate the mechanism of E-V energy transfer to species such as H_2 D_2 and HD.

Digital data analysis along with the very high speed photolysis system has permitted the observation of several decomposition pathways not previously observed in molecular I_2 and the identification of responsible processes.

Research supported by the Air Force Office of Scientific Research.

New Spectroscopic and Kinetic Techniques

The use of Coherent Antistokes Raman Scattering (CARS) is being developed to provide very high speed capability for studies of a variety of transient phenomena in molecular systems. Calculations have shown that the 10^5-10^{10} increase in sensitivity over conventional Raman techniques will enable observation of molecular population dynamics on nanosecond time scales. Studies previously constrained to employ relatively slow infra-red detectors can now be made using high speed visible photomultipliers and the range of species and excited states now accessible for study can be dramatically increased. Very high power short pulse narrow band tunable laser sources are being developed for these studies. The spectroscopic techniques being implemented will have application to studies of solids and liquid as well as gases.

HIGHLIGHTS

1) Second order quenching rate constants have been measured for deactivation of CO(v=1) and $CO_2(00°1)$ by Br_2. It has been determined that in both cases bromine is a relatively slow quencher. Initial measurements using CF_3Br indicate rates on the order of 10^5 sec^{-1} $torr^{-1}$ and using such materials as photolytic sources of $Br^* \ ^2P_{\frac{1}{2}}$ atoms may be less desirable than Br_2.

2) The use of two photon absorption for molecular kinetics observations has been demonstrated in our studies of I_2. Two photon excitation has for the most part in the past been used for spectroscopic studies exclusively. We have demonstrated that two photon excitation can populate otherwise inaccessible molecular states and provide sufficient densities to observe both quenching and predissociation from these new states.

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Picosecond Time Resolution Spectroscopy

Previously a unique picosecond time resolution spectrometer was built. It consists of a tunable laser source that emits a c.w. train of 10 psec duration optical pulses. Luminescence from photo excited samples is interrogated by a non linear optical lightgate system that discriminates in time (with a 10 psec width) and in wavelength (with a 2Å resolution).

The system was upgraded last year and produces now 7-10 psec duration light pulses at a repetition rate of 10^8Hz, tunable between 5650Å and 6400Å and with a peak power of 350 Watt. The output (luminescence intensity vs. time) can now be automatically printed out and mathematically analyzed by a computer which controls the stepping of optical delay lines. This new system allows the averaging of many time runs and has greatly increased the sensitivity of our system. Time varying light signals, like luminescence can be analyzed with the lightgate from 5000Å to more than 8000Å.

1. Time Resolved Study of Highly Photo Excited CdSe Crystals at 4.2°K - In continuation of past achievements in the study of highly photo-excited semiconductors (Cds, CdSe, Zno) we have now used the Picosecond Time Resolution Spectrometer in a study of processes that occur immediately after absorption of a very strong light pulse by CdSe crystals. We have measured the spectral distribution of luminescence radiation emitted by CdSe at 4°K at 0, 50, 100, 150, 200 and more picoseconds after pulse excitation. At high incident light intensities we find a wide luminescence band which narrows in time. At very low light intensities luminescence is emitted in the known bound exciton bands. In addition to this spontaneous emission in backward direction we also observe stimulated emission in some directions at high light intensities. Both processes are seen to interfere with each other. We are presently trying to fit a kinetic model; it also seems likely that at first an electron-hole liquid might exist in CdSe. The observations are clearly contradicting earlier reports of others of the observation of Bose-Einstein Condensation of Bi-excitons in CdSe under very similar conditions.

With computer-print outs of our results we can now very clearly distinguish between exponential, nonexponential, or double-exponential time decays. All these types have been observed under different conditions with CdSe. We have, therefore, a tool now that allows us to study details of reaction kinetics of quasiparticles in direct semiconductors at high excitation densities with decay times in the 10-500 psec range.

2. Viscosity-Dependent Lifetime of Electronic Excitations in Certain Dye Molecules - The fluorescent quantum efficiency of Malachite Green and Crystal Violet, two dyes, was found to be strongly viscosity dependent by Forster and coworkers many years ago. Detailed picosecond resolution, "delayed probe" measurements by Ippen and Shank found that the return to the ground-state, after pulse photo excitation of the first excited electronic state, was indeed viscosity dependent although it was found that ground state recovery occurred with a double exponential decay and slightly different viscosity dependences. We have now studied the viscosity dependence of the luminescent emission of the first excited electronic state and find a double exponential decay in agreement with Ippen and Shank. We are now working on the exact viscosity-dependence of both exponential decay times.

3. Lifetime of the Excited State of Bacterio-Rhodopsin - A recent Scientific American

article (June 1976 by Walther Stoeckenius) starts: "The Purple Membrane of Salt-Loving Bacteria: The color is that of rhodopsin, the visual purple of the animal eye. In halobacterio rhodopsin serves as the pigment of a newly discovered photosynthetic mechanism that converts light into chemical energy."

In collaboration with Professor Aaron Lewis of the Department of Applied and Engineering Physics at Cornell we have studied the lifetime of the photo-excited state of bacterio-rhodopsin at physiological temperatures in patches of purple membrane. We find a lifetime of 15 ± 3 psec. We observe no concentration dependence of the lifetime over the range 1.1×10^{-6}M to 1.0×10^{-5}M. We conclude that the emission which we observe comes from bacterio-rhodopsin and not one of its photo chemically produced intermediates, and that the emission cannot originate from the state into which light is absorbed. These results were accepted for publication in "Biophysical Journal".

4. General Remarks - The measurements of organic dye molecules and in particular of Bacterio-Rhodopsin were mainly done to prove the versatility and usefulness of the spectrometer. In the future separate support and equipment will be used to continue these studies. With funds from this contract we would like to pursue mainly an improvement of the spectrometer towards sub-picosecond pulses and higher peak powers and a continued application of this fast time-resolved spectroscopy to the study of highly photoexcited semiconductors.

Measurements in liquids were made by focussing the modelocked dye laser output into the jet of a continuous flow system of purple membrane patches in solution or solutions of Malachite Green and Crystal Violet. In both cases a fast flow sample avoids problems of thermal effects, saturation and photo-decomposition. With CdSe crystals the laser output was focussed directly onto the surface of the crystals, immersed in liquid helium. As shown, the Picosecond Time Resolution Spectrometer has proven a very versatile instrument of very good sensitivity (bacterio-rhodopsin has a quantum efficiency of luminescence as low as 10^{-4}), great accuracy and enormous stability (runs were made over hours of operation). We believe that this type of instrument will have a great impact on luminescence studies in the picosecond time range for a wide range of materials.

Research supported by the Office of Naval Research and the Materials Science Center.

Nonlinear Spectroscopy

Over the past 5-6 years, and supported by this contract, we have pioneered the measurement of the wavelength dependence of second order optical nonlinear susceptibilities in the excitonic range of semiconductors. Over the years we have shown what can be done, given examples of methods and what can be learned; our equipment, however, is by now quite outdated (one minute waiting time between laser shots, for example). We have, therefore, terminated this project with the study reported below.

A comprehensive study of CdS was finished early during the year and is being written up as a Ph.D. Thesis by Janet Jackel and in the form of various papers. Two papers have already been submitted for publication.

In studying nonlinear properties of CdS at He temperatures with a tunable laser particular emphasis was given to simultaneously monitoring harmonic generation and two-photon absorption. This way the origin of various bands in the exciton region could be ascertained.

In two-photon absorption the fine structure of the P-excitons could be resolved for the first time. The strengths of absorption peaks of P-excitons and their dependence on the polarization of light agree with predictions of a many-band model of two-photon absorption. Additional two-photon absorption peaks were identified as phase matched two-step two-photon processes involving second harmonic polarization.

The second harmonic study provided (together with an earlier, but different measurement by Levin et al) the wavelength dependence of the nonlinear optical susceptibility. A fit to various models could be discussed; in particular it was noted that spatial dispersion had to be added in a very simple way into the model of nonlinear susceptibility for CdS.

Finally, in our application of phase-matched second harmonic generation the upper excitonic dispersion curve of CdS was experimentally determined. For that purpose the phase matching energy, $\hbar\omega$, was determined for various angles of two inclined fundamental laser beams. $\hbar\omega$ and k of the dispersion curve were thus found directly for seven different points. A dispersion model including effects of spatial dispersion is seen to fit the experimental points better than a classical model.

Research supported by the Office of Naval Research and the Materials Science Center.

HIGHLIGHTS

1) The polariton dispersion curve of B-excitons in CdS was measured directly with nonlinear optical spectroscopy for the first time.

2) Time-resolved luminescent spectra were taken of highly photoexcited CdSe crystals in a 10-500 psec time sacale.

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Nonlinear and Electro-Optic Effects

The objective of this program is to study the properties of various nonlinear and electo-optic processes and materials that are important for the generation, modulation, and detection of electro-magnetic radiation from the infrared to the ultraviolet. Efforts during the past year have been concentrated in the following areas: 1) The development of an extremely rapid and efficient electro-optic tuner for dye lasers and methods for producing pico-second tunable radiation for measuring rapid time-varying processes. The work is being extended to semiconductor lasers in the near infrared region. 2) Carrying out detailed theoretical and experimental studies of various photon-assisted and unassisted charge-transfer processes between H^+ and other suitable atoms for the purpose of achieving laser action in the VUV region of the spectrum. 3) Construction of artificial periodic structures to compensate for material dispersion in non-linear optical processes.

Research supported by the National Science Foundation, the Advanced Research Projects Agency, and the Materials Science Center.

Tunable Laser Spectroscopy

Our electro-optically tuned cw dye laser now has a linewidth on the order of 0.02Å and can be used to mode-lock and precisely control high-powered flashlamp-pumped dye laser through the method of injection locking. Efforts are being made to detect very weak high order vibrational transitions in liquids and solids using laser derivative spectroscopic methods.

Research supported by the Advanced Research Projects Agency and the Materials Science Center.

Thin-Film and Integrated Optics

The aim of this program is to study the optical properties of thin films and their potential uses in active and nonlinear optical devices. Specific projects include the generation of ultraviolet second harmonic radiation in thin-films using artificial periodic structures for phase-matching and the study of the optical properties of glass and thin-films doped with rare-earth ions.

Research supported by the National Science Foundation, the Advanced Research Projects Agency, and the Materials Science Center.

HIGHLIGHTS

1. The optical properties, fluorescent lifetime, and method of fabrication of very low-loss and high optical quality Nd^{3+} doped glass thin-films are reported. Substantial optical gain due to stimulated emission in such films is obtained for the first time.

2. Phase-matched second harmonic generation in solid thin-films has been achieved for the first time by using gratings etched onto the surface of a nonlinear substrate to modulate the nonlinear susceptibility.

3. The total scattered electric field of a periodic dielectric optical waveguide is derived in terms of the Green's functions of the unperturbed structure. A condition for self-excitation that takes into account the coupling between radiation and guided modes is obtained in a very general manner; the method is therefore valid for arbitrary periods of the grating structure. Results show that the effect of the coupling between the oscillating guided field and the radiation modes is to change the dependence of the threshold gain on the amplitude of the periodic perturbation: Increasing the depth of the grating beyond an optimum value causes in increase in threshold due to larger coupling to radiation modes.

4. The possibility of mode locking of high-powered laser oscillators by injection locking to a weak mode-locked signal from a cw laser is proposed and demonstrated. The experiment was carried out using a flashlamp-pumped dye laser injection locked to a mode-locked cw dye laser. Gains on the order of 3×10^4 and nearly Fourier-transform limited mode-locked pulses were obtained.

5. A simple two-state molecular theory for calculating the cross section for the photon-assisted charge-exchange collision process $A^+ + B + h\upsilon \rightarrow A + B^+$ is developed. The results demonstrate that considerable enhancement of the charge-exchange cross section may be possible with the moderate field intensities presently available.

6. A VUV lasing scheme employing charge-exchange between H^+ and Cs atoms is discussed. An approximate set of rate equations is described and numerically solved to determine the conditions under which the threshold for laser action might be achieved. The required density and sharpness of both the H^+ and Cs pulses and the expected characteristics of the laser output under various initial conditions are determined from the solution of these equations.

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Tunable Infrared Lasers

The tunable spin flip Raman laser was operated in a configuration in which an external laser mirror was employed. Efforts to achieve lasing with an anti-resonant ring cavity continued. Careful experimental and theoretical analysis indicated that the samples employed so far had excessive pump frequency absorption. Shorter crystals with much lower loss will be installed in August 1976.

The Spin Flip Raman Laser Facility was used to obtain absorption data on NO for S. H. Bauer.

A novel configuration for an infrared analytical instrument was disclosed to the Cornell Patent Office. It is based upon the tunable spin flip Raman laser in which an intracavity cell sample may be located. Very sensitive, high resolution operation is predicted for this instrument.

Stimulated Raman scattering studies from electrons in InSb were initiated late in the year. Tunable scattering was observed in the 5.5-6 micron region.

Research supported by the Energy Research and Development Administration and the Materials Science Center.

Atom Deactivation of Molecular Vibrational Energy

A new technique for measuring atom deactivation was devised during the past year. Gas phase titration for the atom specie will be combined with U.V. resonance fluorescence determination of the titration end point. The end point determination will be done in the laser induced fluorescence cell with no limitation upon the thermal environment. Room temperature calibration of the method with EPR atom concentration determination will be used. Implementation of this technique has begun.

Research supported by the Advanced Research Projects Agency through the Office of Naval Research.

Iodine Atom Laser Studies

The reaction sequence

$$F + HI \rightarrow HF^{+} + I, I^{*}$$
$$HF^{+} + I \rightarrow HF + I^{*}$$

which combines vibrational excitation through chemical reaction followed by V→E transfer to pump iodine atoms was tested in a slow flow apparatus suitable for spectroscopic diagnostics. Analysis of the HF^{+} emission V, R spectra obtained indicated that a high vibrational temperature ($T_V \times 13{,}000K$) was achieved which is suitable for inverting the I*, I system. This reaction sequence is attractive for iodine atom lasers because the V→E exchange partners are premixed and because the V→E transfer is very fast.

Research supported by Army Research Office, Durham.

Electronic to Vibrational Energy Transfer

E→V transfer from $O_2^*(^1\Delta_g)$ to HF and HCl was observed by monitoring the fluorescence following the transfer. Efforts continue to determine the branching ratio of E→V transfer to HF(v=1) and HF(V=2) both of which are found to be excited by O_2^*.

Research supported by the Army Research Office, Durham.

Laser Induced Chemical Reaction

Our study of the four center reaction $HF^+ + D_2 \rightarrow HD + DF$ was completed. Experimental studies coupled with computer modeling substantiated the conclusion that this reaction obeys classical, thermal kinetics and is not significantly vibrationally enhanced.

HIGHLIGHTS

1. E→V transfer from $O_2^*(^1\Delta_g)$ to HF and HCl was observed.

2. A new analytical, spectroscopic method for sensitive, high resolution infrared spectral analysis was developed.

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DEFECT STRUCTURES STUDY GROUP

Lattice defects are the important microscopic components of many important physical processes which are technologically limiting in real materials, such as fatigue, creep, oxidation, precipitation, electric breakdown, optical properties, etc. Characterization and fundamental understanding of the structure and properties of defects will provide the essential basis for the understanding of complex phenomena associated with real materials.

There are three themes which run through the research activities of this Study Group. The first is the structure and properties of grain boundaries in metals, alloys, and ceramic diffraction. Many aspects of this work are unique, since certain of the techniques utilized in the various studies were developed entirely at Cornell. The focal point of much of the research is the use of well characterized grain boundaries, produced by a welding technique in the form of thin bicrystals, which are ideally suited for microscope or diffraction studies. Recently, x-ray diffraction techniques have been developed to study these bicrystals, which potentially allow the determination of the atomic structure of grain boundaries. This recent advance has opened up the entire field of the structure of grain boundaries and much exciting progress is expected in the near future.

The second theme is point defects and radiation effects, including self-interstitial atoms (SIAs), vacancies and clusters of these defects produced by either heavy-metal ion, neutron, or electron irradiation. Radiation-induced (non-Gibbsian) segregation effects are studied as is the role of interstitial gas atoms in the stabilization of clusters of self-interstitial atoms and vacancies. Field-ion and atom-probe microscopy are the main experimental techniques.

The application of these highly direct observational techniques allow a correlation to be made between the local defect structure and chemistry on a scale (a few angstroms) that is not presently possible with any other technique. The ultra-high vacuum time-of-flight (TOF) atom-probe field-ion microscope (FIM) constructed at Cornell was specifically designed for the study of defect structures in metals.

The third theme is hydrogen in metals, including niobium, palladium, iron, and metals suited for field-ion and atom-probe microscopy work. The major experimental techniques are nuclear magnetic resonance for the niobium and palladium, permeation for iron and steels, and atom-probe field-ion microscopy. Diffusion, interaction with solutes and with second phases are among the topics studied.

Defect Structures Study Group Membership

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B. W. Batterman, Applied and Engineering Physics and Materials Science and Engineering
R. M. Cotts, Physics
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H. H. Johnson, Materials Science and Engineering
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Electron Microscope Studies of Grain Boundary Structure in Cubic Metals

Efforts have been made to gain information about secondary grain boundary relaxations in cubic metals by electron microscopy. The work has been aimed at determining the extent to which ordered boundaries, possessing periodic structures of different possible types, exist. There has been much speculation that such boundaries are of relatively low energy and therefore should be stable under certain conditions. Specific projects underway include: (1) search for secondary grain boundary dislocation relaxations in Coincidence Site Lattice boundaries: (2) search for secondary networks in Near-Coincidence boundaries: (3) detection of line structure due to secondary relaxations in Plane Matching boundaries: (4) studies of the faceting and the preferred orientations of grain boundaries during annealing.

Research supported by the Energy Research and Development Administration.

On the Structure of Low Angle (110) Twist Boundaries and its Relationship to the O-Lattice

The dislocation structure of low angle (110) twist boundaries in thin film bicrystals of gold was studied by transmission electron microscopy. The structure was found to consist of a dislocation network with hexagonal mesh openings. Also, the various dislocation segments possessed non-coplanar Burgers vectors. The results were discussed in terms of the O-Lattice construction of Bollmann, and it was found that the structure could not be derived from a simple O-Lattice based on a homogeneous transformation connecting to two rotated crystal lattices. Instead, it was necessary to employ an inhomogeneous transformation which involved displacements normal to the boundary plane (i.e., parallel to the twist axis). These results emphasize the fact that the O-Lattice approach to low angle boundary structure may not be straightforward. In general, both simple homogeneous transformations and inhomogeneous transformations must be considered, and there is no simple way to predict which may actually apply. Such procedures are equivalent to a search for the dislocation network of minimum energy.

Research supported by the National Science Foundation and the Materials Science Center.

Grain Boundary Diffusion of Silver Through Gold Thin Films

The diffusion of silver solute atoms along grain boundaries in gold thin films is being studied using a surface accumulation technique. Polycrystalline gold thin films possessing a columnar grain structure are first prepared. A layer of silver atoms is then evaporated on the bottom surface *in situ* in vacuum, and the specimen is heated to the diffusion temperature. The

silver atoms then diffuse along the transverse grain boundary short-circuits and spread out on the opposite (exit) surface. The average concentration of silver atoms reaching the exit surface is then measured in situ by Auger spectroscopy. The technique is exceedingly sensitive, since the diffusion distance is short (~1000Å), a large number of grain boundaries is present (grain size <1μ) and the Auger spectrometer can readily detect $\sim 10^{-2}$ of a monolayer of silver. With this technique grain boundary diffusion rates can be measured at unusually low temperatures under conditions where lattice diffusion is essentially frozen out. Calculations of the diffusion kinetics have been carried out taking into account diffusion on both the entrance and exit surfaces and in the grain boundaries. Experiments have been performed involving diffusion in general polycrystalline films and also in films containing pure tilt boundaries of controlled misorientation which have been prepared by a novel method developed in our laboratory.

Research supported by the Energy Research and Development Administration.

Serration of Edge Dislocations in Low Angle Symmetric Tilt Boundaries in Gold

A fine structure of the edge dislocations in low angle symmetric tilt boundaries in gold that has not been previously reported was studied in thin-film bicrystal specimens using transmission electron microscopy and diffraction. In (100) symmetric boundaries with tilt angles $\leq 9°$ the dislocations were serrated with segments parallel to <110>; in (110) symmetric boundaries with tilt angles $\leq 7°$ the dislocations were also serrated but with segments parallel to <112>. The detailed geometry of the serrations depended on the direction of the tilt axis in the boundary plane but was always such that the dislocations, on average, ran parallel to the tilt axis, in agreement with standard models. These configurations, while increasing the dislocation line length, allow the dislocation to dissociate on {111} planes into partial dislocations and stacking fault ribbons. Evidently the latter factor is energetically dominant and the observed structures should be a general feature of symmetric tilt boundaries in materials with low stacking fault energies. Tilt boundaries of the types investigated in the present work have been employed in previous studies of dislocation pipe diffusion rates. The new information gained about the dislocation core structures is relevant to these measurements, and this aspect of the experimental results will be discussed.

Research supported by the National Science Foundation and the Materials Science Center.

On Dislocation Behavior at Advancing Grain Boundaries During Recrystallization

A systematic discussion has been given of dislocation behavior at an advancing grain boundary during recrystallization. For this purpose it is convenient to separate both lattice and grain boundary dislocations into "intrinsic" and "extrinsic" types. The decomposition of lattice dislocations into grain boundary dislocations as they impinge upon the advancing boundary is then described, and the various special relationships which should exist between intrinsic and extrinsic types are discussed.

Research supported by the Energy Research and Development Administration.

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Diffuse X-Ray and Mössbauer Scattering

The room temperature studies have been published. We are continuing studies of NbZr at low temperatures and are attempting to measure the profile of the quasielastic central peak by Mössbauer spectroscopy.

Anharmonic Vibrations of Nuclei and Valence Electron Distributions in Solids

We are building apparatus to pursue x-ray studies on higher order forbidden reflections using the Cornell 12GeV synchrotron. A dual-beam line facility is being constructed and preliminary experimental runs have established the feasibility of the measurements.

These projects are supported by the National Science Foundation and the Materials Science Center.

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Atomic Transport: Hydrogen in Metals

During the 1975-1976 year all of the research effort of the group was devoted to study of mobility of hydrogen in transition metals.

1. New direct measurements of diffusion of hydrogen in Pd-Ag alloys were completed and compared with published values of permeation rates for typical concentrations of Ag in Pd. The marked increase in permeation due to addition of Ag is shown by the NMR experiments to be due principally to increased solubility of hydrogen rather than to increased diffusivity. This work is part of a continuing collaboration with Professor E. F. W. Seymour of the University of Warwick, England, which was initiated during his one year visit to our laboratory and concluded in August 1976.

2. W. D. Williams developed and demonstrated a new NMR pulsed field gradient technique for measuring diffusion constants without systematic error due to background gradients. These background gradients are due to inhomogeneous sample magnetization in powder samples usually used for NMR work in metals. Previous NMR experimental measurements suffered from this error, and even though some estimates of correction factors could be made, the effects of background gradients were believed to be the chief source of experimental error in samples having relatively large magnetic susceptibility.

The technique involves placement of two identical field gradient pulses into a modified Carr-Purcell spin-echo pulse train. The time spacing of pulses are varied by steps of four radio frequency pulses and the echo is observed, as signal, at one fixed time. Williams showed that under these conditions echo amplitude depended upon the diffusion coefficient and experimentally controlled variables but not upon the background gradients. The technique was tested in various NbH_x samples known to have large and small background gradients.

3. In the preparation of hydride samples having vapor pressures exceeding one atmosphere, a stainless steel gas rack was constructed and instrumented by L. Bustard for pressures up to 1000 psi. He also tested the NMR spectrometer for its capability to measure $T_{1\rho}$, the spin lattice relaxation time in the rotating frame. Measurements of $T_{1\rho}$ will be useful in following mobilit of hydrogen to temperatures well below room temperature.

We have also initiated a series of NMR observations of deuterium in transition metals at high temperatures (in the α and α' phases). The goal here is to measure the isotope effect for hydrogen diffusion in high hydrogen concentrations. What is being found is that the transverse relaxation times of deuterium in niobium and palladium are unusually short in complete disagreement with expectations. We have initiated a series of experiments to identify the interactions responsible since they might prohibit use of NMR in measuring the hydrogen diffusion isotope effect. Their understanding could be related to the metallurgy of these materials and could result in new insight.

Research supported by the National Science Foundation and the Materials Science Center.

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Diffraction Studies of the Structure of Grain Boundaries

It was demonstrated at Cornell that small and large angle grain boundaries act as a diffraction gratings, giving rise to extra reflections which are related to the periodic structure of the boundary. The initial work involved electron diffraction, and recently it was shown for the first time that x-ray diffraction techniques could be used to examine grain boundaries. This unique technique is being applied in the following areas;

1) The study of the core structure of screw dislocations and the plane spacing in the vicinity of small angle grain boundaries.

2) The study of the structure of large angle grain boundaries.

3) The study of segregation to grain boundaries.

4) The study of the structure of grain boundaries as a function of temperature, as a means of searching for a postulated grain boundary phase transformation.

Research supported by the National Science Foundation and the Materials Science Center.

Phase Transformations, the Local Structure and Atom Imaging in Ti and Zr B.C.C. Alloys

Over the past few years an extensive study has been carried out of the omega phase transformation which occurs in Ti and Zr b.c.c. alloys using electron microscope and diffraction techniques. Direct lattice imaging has been used to examine the early stages of the transformation. Many Ti and Zr-base alloy systems exhibit a characteristic diffuse scattering distribution from the untransformed b.c.c. solid solution. The structure of a new type of defect in the b.c.c. phase has been determined using the diffuse scattering observations on Zr-Nb alloys. This defect was shown to consist of a vacancy about which are rows of atoms displaced along one <111> direction. The similarity of the structure of this linear defect to that of the omega phase suggests that it plays a role in the mechanism of the transformation, which is not yet understood. High resolution electron microscope techniques are being used in an effort to directly observe this defect and thereby, directly verify its existence.

High resolution dark field micrographs obtained from these alloys show images with atomic dimensions. It is possible that the atomic level contrast results from either individual or small clusters of point defects. Theoretical calculations of the contrast from point defects have been carried out, in order to determine the origin of the observed contrast, and examine the possibility of the direct imaging of point defects in crystals.

Research supported by the Materials Science Center.

HIGHLIGHTS

1. Diffraction Studies of the Structure of Grain Boundaries

A. It was demonstrated for the first time that grain boundaries can be studied using x-ray diffraction techniques. Thin film gold bicrystal specimens containing small-angle twist boundaries were examined with Cu K_α radiation, and arrays of extra reflections in the vicinity of f.c.c. reflections were detected. The relative intensities of the extra reflections were in qualitative agreement with structure factor calculations.

B. Further work demonstrated that the structure of large angle grain boundaries can also be studied using x-ray diffraction techniques. A gold bicrystal specimen containing a large-angle <001> twist boundary was examined with Cu K_α radiation and the presence of extra reflections associated with the O-lattice and coincidence site lattice (CSL) of the boundary was detected. The relative intensities of the O and CSL reflections were discussed in terms of the displacement field associated with the twist boundary. In order to obtain an appreciation of the magnitude of the scattering from the boundary, calculated structure factors for small and large angle twist boundaries were compared to the structure factor for single (001) planes of gold atoms. It was then seen that the weakest reflections detectable from the boundary correspond to the scattering from one-seventh of a monolayer of gold atoms, which suggests that the x-ray technique used here may also be applied to study the surface structure of thin films.

C. In a recent paper an electron diffraction technique was developed to study the structure of the high angle <001> twist boundaries. Extra reflections (O-reflections) were observed which were attributed to the diffraction from a periodic displacement field in the boundaries. In order to demonstrate that these reflections were not produced by double diffraction by the two crystals adjoining the boundary, a limited analysis of the double diffraction possibilities was performed. In order to put this technique on a firmer footing a more general analysis was developed in the present work which considers the contribution by double diffraction of all possible combinations of crystal reflections to the experimentally observed O-reflections. It was shown that for all twist boundaries it is geometrically possible for double diffraction to contribute to the O-reflections, under the assumption of an Ewald sphere of infinite radius. It was then demonstrated that when the curvature of the Ewald sphere is taken into account, the possibility of double diffraction can be discounted. Additional experimental work was cited to confirm this conclusion.

2. Phase Transformations, the Local Structure and Atom Imaging in Ti and Zr B.C.C. Alloys

A. Many Ti and Zr-base alloy systems in which a metastable structure called the omega phase is formed, exhibit a characteristic diffuse scattering distribution from the untransformed b.c.c. solid solution. These diffuse scattering observations indicate that a localized defect is present in the b.c.c. solid solution. In the present work the structure of a new type of defect in the b.c.c. phase was determined using published diffuse scattering observations for a Zr-20wt. pct. Nb alloy. The defect was shown to consist of a vacancy about which are rows of atoms displaced along one <111> direction. The particular <111> displacements that occur on opposite sides of the vacancy give rise to structures that are similar to two subvariants of the omega phase. This sequence of subvariants and the additional small displacements normal to the <111> direction can explain the observed diffuse peak shifts characteristic of many Ti and Zr alloy systems. On the basis of the diffraction analysis alone it is not possible to state that the defect structure arrived at is unique. However, this structure does provide the best fit to the observations of all the models tried, and it explains in a physically reasonable manner many of the details of the diffuse scattering. The similarity of this new defect to the omega phase, suggests that it plays an important role in the mechanism of the omega phase transformation. What this role is, still remains to be determined.

B. Images with dimensions of 3-5Å were observed in the tilted beam dark field mode

using the diffuse scattering from b.c.c. Zr-Nb alloys. In an attempt to identify the origin of the image contrast, computer calculations were made of the dark-field images from various crystalline defects with atomic dimensions. For the experimental conditions of this study, the calculated image profile for a vacancy had a width at half maximum of $\sim 3\text{Å}$ and a peak intensity of 6×10^{-4} of the incident intensity. The measured intensities from the observed images were in the range of 4×10^{-3} to 1.2×10^{-2} and a comparison of the calculated and experimental values showed that the observed images could not have resulted from the simple defects used for the contrast calculations. The present status of this work is that the observed contrast results either from another type of crystalline defect, possibly associated with the phase change in this alloy system, or from a surface film on the thin foil specimen. Some experimental evidence exists to reduce the possibility of the latter, while preliminary image calculations demonstrate that higher intensities can occur for a newly proposed defect structure. It is suggested that the best chance for success in the direct imaging of point defects would be achieved by using the dark field mode with a heavy element specimen having a defect with a large strain field.

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An In-Situ Field-Ion Microscope Study of Ion-Irradiated Tungsten and Tungsten Alloys

1. The Recovery Behavior in Stages I and II of Pure Tungsten

The low-temperature field-ion microscope (FIM) isochronal annealing spectrum of pure tungsten irradiated in-situ with 30 keV W^+ ions to a standard dose of $5 \cdot 10^{12}$ ions cm^{-2} at 18K had been shown by Scanlan, Styris and Seidman and Wilson and Seidman to consist of distinct recovery peaks at ∿38, 50, 65 and 80K with a small amount of recovery observed up to 120K. They ascribed a process of self-interstitial atom (SIA) long-range migration in Stage I to the 38K peak and calculated an enthalpy change of migration of 0.085eV for the SIA. However, recent internal friction results published by Okuda and Mizubayaski implied that the process of SIA long-range migration occurs at ∿15K. In addition, a dose and impurity concentration dependent recovery substage in tungsten between 24 and 30K had recently been reported by Dausinger and Schultz in Stuttgart, and they ascribed this substage to uncorrelated long-range migration of an SIA. To investigate the possibility of the existence of SIA long-range migration below 30K the experiments of Scanlan et al. and Wilson and Seidman were carefully repeated. The experimental procedure was modified to allow for a lower irradiation temperature (T_i=6K) and a slower heating rate <2K min^{-1}. The results of the FIM isochronal annealing experiments indicate that there is no appreciable recovery below 20K. This observation is not consistent with the internal friction results of Okuda and Mizubayaski. However, an analysis of the isochronal annealing experiments revealed that the observed recovery between 20 and 40K is too broad to represent a single thermally-activated diffusion process. This conclusion was reached by superimposing an analytical recovery curve, based on a diffusion treatment of the FIM situation, on the FIM isochronal recovery peak centered at 39K. Further details are available in the M.S. Thesis of C.H. Nielsen.

2. The Recovery Behavior in Stages I and II of Tungsten-(Rhenium) Alloys

Direct evidence for the formation of SIA-rhenium atom complexes in 30keV W^+ ion-irradiated tungsten-(rhenium) alloys in Stage I had been reported by Wilson and Seidman. They observed a radical suppression of the 38K substage of the FIM isochronal annealing spectrum as a result of the addition of rhenium to tungsten. In order to determine the kinetics of the detrapping mechanism a search for the release temperature was carried out using the isochronal FIM annealing technique. Tungsten specimens, alloyed with 1 or 3 atomic % rhenium, were irradiated in-situ with 30keV W^+ ions at 15K to a standard dose of $5 \cdot 10^{12}$ ion cm^{-2} and were subsequently annealed to ∿2.5K min^{-1}. The FIM isochronal recovery spectra were observed to contain no unambiguous release peaks analogous to those reported by Wei and Seidman for Pt-(Au) alloys. This result indicated that the SIA-rhenium atom complex had a binding enthalpy of at least 0.8eV.

Post-anneal pulse-field evaporation experiments revealed several isolated complex-contrast patterns randomly distributed throughout the sampled volume of the specimen. A total of $1 \cdot 1 \cdot 10^5$ atoms were counted and 11 complex patterns observed, thus implying a concentration of $\sim 1 \times 10^{-4}$ at.fr. These patterns were different from any of our earlier strain-field contrast effects; they were also different from both the Stage I SIA and the rhenium atom contrast patterns. However, the patterns

were somewhat similar to those observed by Wilson and Seidman in 2.35 MeV electron-irradiated tungsten; Wilson and Seidman irradiated their specimens just below stage III (≈430K) to a close-pair concentration (before recombination) of $\sim 4 \times 10^{-3}$at.fr. and examined them at 18K; it was found that the tungsten specimens contained a complex pattern concentration of 1×10^{-4}at.fr. These researchers suggested that the unusual patterns resulted from either SIA clusters or SIA-impurity atom clusters. It was therefore concluded that the tungsten SIAs remained trapped up to ~400K and that the complex contrast patterns represented a direct observations of the tungsten SIA-rhenium atom clusters.

Research supported by the Energy Research and Development Administration.

The Study of Stages I to IV of Irradiated or Quenched Tungsten and Tungsten Alloys by Field-Ion Microscopy: A Review

A review article was prepared for the International Conference on "Fundamental Aspects of Radiation Damage in Metals" held in Gatlinburg, Tennessee from October 5 to 19, 1975. In this article the progress made at Cornell since 1972 in applying the Quantitative FIM technique to the study of point defects in irradiated tungsten and tungsten alloys or quenched tungsten was reviewed. The emphasis had been placed on ascertaining recovery mechanisms for the major recovery stages which are consistent with both other FIM observations as well as observations employing more macroscopic techniques; hence point defect recovery models were presented for recovery Stages I to III. The following conclusions were reached; (1) the value of the volume change of migration (Δv_i^m) for the Stage I SIA is less than $0.02\Omega_a$; (2) a strong SIA long-range migration peak was found at ~38K; (3) Stage I must terminate at ≤45K and not 100K as had been suggested by earlier researchers; (4) the maximum possible downward T shift of the 38K peak was <10K due to the $p\Delta v_i^m$ effect; (5) the isochronal recovery spectra of four different purity levels (R=15 to 5×10^4) of 30keV W^+ ion-irradiated W were essentially identical between 18 and 120K; (6) these four different purity level W specimens exhibited a distinct series of long-range migration recovery peaks at ~38, 50, 65 and 80K with a small amount of recovery observed up to 120K; (7) conclusions (5) and (6) indicate that the distribution of SIAs produced by the 30keV W^+ ion irradiations was such that the SIAs only interacted weakly with the impurity atoms and that the SIA-SIA reaction dominated the recovery behavior; (8) the long-range migration peaks fit a diffusion-limited annealing model; (9) the FIM experiments provided direct evidence for the long-range migration of both SIAs and SIA clusters in Stage II between ~45 and 120K; (10) the FIM observations of SIA long-range migration in Stages I and II are in agreement with the Dausinger-Schultz results if a T shift of ~5 to 6.5K is made to superimpose the long-range migration peaks in the two sets of data; (11) the binding enthalpy of an SIA to a C atom is ~0.03eV and the binding enthalpy of an SIA to a Re atom is >0.8eV; (2) no unambiguous evidence has been found for isolated thermally converted SIAs (the Stage III SIA) at a concentration about 5×10^{-6}at.fr. at T_i=430K for W electron irradiated to a dose of $\sim 1 \times 10^{20}$cm^{-2}; (13) it was argued that in the Attardo et al. experiments that the transmutation of W to Re, as a result of a thermal neutron dose of $\sim 10^{20}$cm^{-2}, caused a large number of SIAs to become trapped at Re atoms and that the contrast effect they observed after a 60°C irradiation was due to a Re-SIA complex; and (14) the W quenching experiments of Kunz and Schultz, Gripshover et al. in conjunction with the prequenching and electron irradiation experiments of Kunz et al. and the combined FIM-resistivity study of Park et al. indicate that the quenched-in resistivity increment may consist of mainly dispersed impurity-atoms, vacancy-impurity atom clusters and a small concentration of monovacancies.

Research supported by the Energy Research and Development Administration.

Field-Ion Microscope Studies of the Defect Structure of the Primary State of Damage of Irradiated Metals: A Review

A review article was prepared for the "Materials Science Seminar: Radiation Damage in Metals" held at the Materials Science Symposium in Cincinnati, Ohio on November 9th and 10th, 1975. This paper reviewed the application of the FIM technique to the problem of determining directly the spatial distribution of point defects produced by an energetic primary knock-on atom. Attention

was focused specifically on the primary state of damage (i.e., the point-defect distribution without a post-irradiation anneal) produced by energetic heavy-ions (e.g., 20-100keV W^+, Xe^+ or Ar^+) and fast neutrons (energy > 1MeV) in the metals tungsten, iridium and platinum; the simpler primary state of damage produced by MeV electrons was not considered. A review was first given of the theoretical concept of a depleted zone and the role played by both focusons and focused replacement collision sequences in its development. It was emphasized that the FIM technique is the only one presently capable of determining the spatial distribution of point defects within and around a depleted zone.

The Cornell FIM research on depleted zones was reviewed in detail. The emphasis in this work was on determining the point-defect structure of a depleted zone produced by a single ion. The irradiating ion used was the self-ion (W^+) to avoid any possible problems associated with the introduction of impurity atoms in the lattice as a result of the irradiation. Each depleted zone was created in an almost initially perfect crystal lattice (i.e.,the tip volume of $\sim 10^{-16} cm^3$). Two different irradiation temperatures (T_i) were employed; 473 and 18K. The T_i of 473K is towards the top of Stage II and is therefore above the temperature of long-range migration of the Stage I SIA, but below the temperature where monovacancies migrate.

The work of other groups on the primary state of radiation damage in the metals tungsten, iridium and platinum was also reviewed. The emphasis of most of this work had been on characterizing the distribution of vacancy damage produced at room temperature, and in a few experiments, at 78K. Typically only large clusters of vacancies (i.e., greater than 10 vacancies) had been studied as the minimum field evaporation increment, for a high index plane, was one atomic layer. This coarse an increment precludes, almost a priori, obtaining detailed information about the point-defect structure of a depleted zone. Nevertheless, this research has been useful in demonstrating that basically three morphological types of vacancy damage exists in the primary state of damage. These three basic types are: (1) depleted zones; (2) compact vacancy clusters; and (3) dislocation loops. The dislocation are depleted zones that have collapsed into the lower-energy dislocation loops.

The important result that emerges from the FIM research on both tungsten and iridium is that the dislocation loop portion of the damage accounts for only a small fraction of the total vacancy population. The remaining fraction of the vacancy population (90% in the case of tungsten) is in the form of depleted zones (with a vacancy concentration of between 1 and 20at.%) and compact clusters. These observations offer an explanation of why the yield factor (Y), where

$$Y = \frac{\text{observable vacancy loops (number per cm}^2\text{)}}{\text{ion dose (number of ions per cm}^2\text{)}}$$

measured by TEM is often less than unity. For example, in the case of copper irradiated with 30keV Cu^+ ions at room temperature Y is 0.3, and in the case of tungsten irradiated at room temperature it is 0.1. This is an important point because the TEM technique has been extensively used to study vacancy damage in both self-ion and neutron irradiated metals. The observation of the primary radiation damage state by TEM depends heavily on the ability of the vacancy-rich core of a depleted zone to collapse into a dislocation loop with sufficient strain-field contrast to make itself "visible" in an electron microscope image. Thus, the FIM observations provide a simple explanation of the low yield-factor, determined by transmission electron microscopy, for a number of ion-irradiated metals.

Research supported by Energy Research and Development Administration.

An In-Situ Field-Ion Microscopy Study of the Recovery Behavior of Ion-Irradiated Molybdenum in Stages I and II

The mobility of single molybdenum SIAs was studied in a series of in-situ FIM experiments. High purity (resistivity ratio of ~5700) molybdenum specimens were irradiated with 30keV Mo^+ ions to a standard dose of $5 \cdot 10^{12}$ ions cm^{-2} at 10K. Subsequent isochronal annealing experiments were

performed at a heat rate of $\sim$2.5K min^{-1} between 10 and 120K. The low temperature annealing spectrum was shown to consist of distinct recovery peaks at 32, 45 and 70K. The major peak at 32K was considered to represent the onset of long-range migration and was found to closely obey the analytical shape predicted by a diffusion model. The effect of the imaging electric field on the mobility of the SIA was studied in a series of control experiments. The results of these experiments demonstrated that the SIA was mobile at 40K in the absence of the electric field, and that the large electric field required by the FIM technique had only a minimal effect on the annealing kinetics of the SIA in molybdenum. Further details may be found in the M.S. thesis of C. H. Nielsen.

Research supported by the Energy Research and Development Administration.

A Field-Ion Microscope Study of the Recovery Behavior of Stage II in Ion-Irradiated Platinum - 0.10, 0.62 and 4.0at.% Gold Alloys

A detailed FIM study of the recovery behavior of Stage II in ion-irradiated Pt-0.10, 0.62 and 4.0at.% Au alloys has been performed. Typically an FIM specimen was irradiated with 30keV W^+ or Pt^+ ions at $\leq 2.10^{-9}$Torr and at a tip temperature between 35 and 40K. The specimen was then warmed to $\geq$100K at a warming rate of $\sim$1.5K min^{-1} and the specimen's sureface was examined for the presence of SIA contrast effects. The recovery spectrum for each alloy consisted of two distinct peaks at $\sim$68 and 88K. The surfaces of five irradiated pure Pt specimens [$\sim(1\text{-}2)\cdot10^{-5}$at.fr. impurity level] were also examined to demonstrate that the recovery spectra observed are only characteristic of the Pt-(Au) alloys. The observed recovery spectra are most likely due to the dissociation of SIAs from Au atoms. Further details may be found in Materials Science Center Report No. 2398.

Research supported by the Energy Research and Development Administration.

A New Technique for Focused Collision Sequence Range Measurements

One of the most persistent problems in the field of radiation damage is that of understanding the nature of the initial damage event; i.e., the spatial distribution of vacancies and self-interstitial atoms produced as the result of the impact of an energetic particle. Since Silsbee first introduced the concept of focused collision sequences (FCS) in 1957, these events have often been discussed as a determining factor in the inital spatial distribution of damage. However, due to experimental difficulties, the range of these events, and even proof of their existence, has remained somewhat elusive. Indeed in gold, FCS ranges of <50Å to 4000Å or more have been proposed. Clearly, further work is needed to rationalize this immense disparity, and in a more general sense to understand the role of focusing in radiation damage. Toward this end we have developed a unique, and direct technique for studying focused collision sequences.

The present series of experiments is being carried out on gold, although the technique should be applicable to other metals as well. The specimens are epitaxially grown, vapor deposited single crystals which range from 100 to 1500Å in thickness. Experiments to date have been carried out on crystals with <100> film normals, but films of other orientations (<110> and <111>) are now being prepared in order to study crystallographic effects. The films are bombarded with low energy ($\leq$700eV) Xe^+ ions directed along the film normal. Focused collision sequences with a range greater than the film thickness can cause the ejection of atoms as ions from the bottom surface of the film. These ions are detected using a Bendix Channeltron Electron Multiplier Array (CEMA) system which consists of two individual CEMAs placed in series. The output from this is detected both visually (with a fluorescent screen) and electronically. The experiments are carried out in a high vacuum system ($\sim5\text{x}10^{-8}$Torr). The specimen holder is mounted on the tail secton of a continuous transfer liquid helium cryostat, with which the specimen can be maintained at any temperature between 25 and 300K. In order to ensure that the observed current emerging from the bottom surface of the film is not due to channeling of light neutral or ion impurities (H, H^+, or He, He^+) a crossed magnetic and electric spectrometer is placed in the beam path. This spectrometer removes any light neutral or ion component from the beam.

The irradiating Xe^+ ion beam is pulsed at a known frequency ($\sim$100 Hz) by pulsing the

ion-gun filament bias. Each pulse produces a burst of separate events in the CEMA; every burst is caused by a simple ion emerging from the bottom surface of the film. These events are individually amplified and then averaged and fed into an Ithaco model 391A lock-in amplifier (LIA), operating at the 100 Hz ion pulse frequency. This synchronous detection system given a very precise measure of the detector output, with a high decree of noise rejection. Since the output is proportional to the input ion current, the variable of interest is the ratio of the output to this current, This is provided directly by a current measuring circuit linked to a ratiometer built into the LIA. Both this ratio and the direct LIA output are recorded on a dual pen strip chart recorder.

The system described above is presently being used to measure yield factors (the ratio of the output to input ion current) as a function of the thickness of the gold films at constant irradiation temperature, incident ion energy and film orientation. This type of experiment yields the range distributon of FCSs.

Research supported by Energy Research and Development Administration.

Atom-Probe Field-Ion Microscopy

1. Technical Improvements in the Atom-Probe FIM

(a) Resolution

Several technical improvements have been made in the atom-probe FIM and in the operational technique which have improved the resolution of the instrument. The improvements were as follows: (1) The design of the digital timer was modified to eliminate systematic timing errors; (2) Tracking power supplied for the dc and pulse voltages were installed; and (3) the regularly obtainable background vacuum was reduced from $\leq 10^{-8}$Torr to $\leq 5 \times 10^{-10}$Torr. This third point is important because it reduces the number of artifact effects caused by the interaction of residual impurity gases interacting with the specimen.

(b) Low-Energy Ion-Gun

A preliminary experiment testing the performance of the low-energy gas ion-gun was conducted. A tungsten specimen maintained at 30K was irradiated with 275eV Ne^+ ions. After the removal of the damaged surface layer by field-evaporation an isochronal annealing experiment was performed. This latter experiment revealed the presence of SIAs migrating to the surface of the FIM tip. These SIAs were most likely produced at 30K by the focused replacement collision sequence mechanism. This preliminary experiment suggests two avenues of research. First, range measurements of focused collision replacement sequences can be directly measured. It is also possible to determine the energy and temperature dependence of the range by this same technique. Second, it is clear that the interaction of SIAs with impurity atoms can also be studied by the atom-probe technique where the SIAs are introduced by low-energy bombardments.

(c) Residual Gas Analyzer

A Uthe Technology Inc. (UTI) Model 100C residual gas analyzer was installed on the atom-probe FIM. The analyzer allows us to determine the composition of the residual gases in the vacuum system. This instrument has proved to be particularly valuable for determining whether specific impurity atoms originated in the specimen or were artifacts of the vacuum conditions.

2. Results

A number of pure metals and alloys have been examined in the atom-probe FIM including tungsten, tungsten-rhenium, molybdenum, molybdenum-titanium, TZM (titanium-zirconium-molybdenum) alloy, and a low swelling stainless steel (LSIA).

(a) Tungsten and Tungsten Alloys

Tungsten and tungsten alloys were investigated to develop an operational technique that would be suitable for experiments on the neutron irradiated samples of tungsten and tungsten-rhenium. First, in the case of the pure tungsten specimen the five naturally occurring isotopes of tungsten (W^{180}, W^{182}, W^{183}, W^{184} and W^{186}) can be readily distinguished from one another. The W^{+3} spectrum was recorded with the atom-probe FIM at a background pressure of 6×10^{-10}Torr and tip temperature of ~25K. The drift distance of the ions in the flight tube was 1600.3mm. A comparison of our experimental W^{+3} isotopic abundances with the handbook values of these quantities demonstrated rather good agreement.

A W^{+3} and R^{+3} spectrum for a W-25at.% Re alloy was recorded at a tip temperature of 25K employing a drift distance of 2232mm. The $^{185}Re^{+3}$ peak at 61.67amu and the $^{187}Re^{+3}$peak at 62.33.amu were resolved. This experiment indicated that the resolution of out time-of-flight atom-probe FIM is close to a $\Delta m/m$ value of ~1/200. Composition profiles obtained from the W25at% Re specimens yielded an average Re concentration which was close to the nominal value of 25at.%Re.

(b) Molybdenum and Molydbenum Alloys

In preparation for a study on a series of neutron irradiated molybdenum alloys a number of preliminary experiments on molybdenum and molybdenum alloys were performed. Because the amount of irradiated material is very limited extensive specimen development was performed on commercial samples of molybdenum and a titanium-zirconium-molybdenum (TZM) alloy. After developing a successful FIM specimen preparation technique for molybdenum and TZM, runs were made on these materials to test that the atom-probe FIM experiments were possible. The titanium and zirconium were clearly distinguishable from one another and the measured concentrations agreed with the nominal concentrations. The same techniques were also successfully applied to the as-received, unirradiated samples which serve as controls for the neutron-irradiated specimens.

(i) Molybdenum

The peaks associated with the seven naturally occurring isotopes of Mo (Mo^{92}, Mo^{94}, Mo^{95} Mo^{96}, Mo^{98}, Mo^{100}) were clearly distinguishable from one another. The Mo^{+2} spectrum was recorded with the atom-probe FIM at a background pressure of 5×10^{-9}Torr, and at a tip temperature of ≈60K; the drift distance was 2213mm. A comparison of our experimental Mo^{+2} isotopic abundances with the handbook values of these quantities showed that there was good agreement between the two sets of values.

(ii) Titanium-Zirconium-Molybdenum (TZM)

The $^{90}Zr^{+3}$ peak was readily distinguished form the Mo^{+3} peaks. The Zr^{+3} isotopes ^{92}Zr, ^{94}Ar and ^{96}Zr clearly cannot be distinguished from the Mo^{+3} isotopes ^{92}Mo, ^{94}Mo and ^{96}Mo. No evidence was found for the ^{91}Zr in the +3 charge state. This isotope should have appeared at 30.33amu. It did not appear, most likely because its isotopic abundance is only 11.23% compared with an isotopic abundance of 51.46% for the ^{90}Zr isotope; thus we could expect only ~1 event for this isotope in the +3 charge state for the total number of Mo^{+3} ions counted (≤10,000). Analysis of the spatial distribution of the titanium and zirconium showed that the titanium was randomly distributed while all the zirconium was contained in a single cluster. This single cluster of zirconium was detected just before the tip failed, and could have contributed to the failure of the tip. These experiments on TZM indicated that both the titanium and zirconium alloying elements in the ≤1at.% concentration range could be detected and that the techniques developed should work reasonable well for irradiated specimens.

(iii) Molybdenum-(Titanium)

Atom-probe FIM experiments were performed on unirradiated specimens of the Mo-0.5wt.% Ti alloys. The Mo-0.5wt.% Ti alloys exhibited an enhanced swelling behavior when compared to the molybdenum specimens irradiated under identical conditions to the same fast neutron dose. It is the purpose of the present experiment to determine the role played by the titanium in the swelling behavior of neutron irradiated molybdenum. The five isotopes of Ti (Ti^{46}, Ti^{47}, Ti^{48}, Ti^{50}) were very clearly resolved. The Ti was also found to be randomly distributed throughout the alloy. This is significant because a comparison of the present results with the results on the irradiated Mo-(Ti) alloys should allow us to comment in detail on the changes produced in the spatial distribution of Ti atoms in the alloy as a result of the fast neutron irradiation.

(c) A Low Swelling Stainless Steel Alloy (LSIA)

A low swelling stainless steel alloy (LSIA) developed at the Oak Ridge National Laboratory (ORNL) has been analyzed by the atom-probe FIM technique. To date we have restricted our work to unirradiated speciments of this alloy because of the high radioactivity of the neutron irradiated specimens. The alloy LSIA contains 2.06at.% Si and 0.16at.% as swelling inhibitors. The composition of each element in this alloy as determined by the atom-probe FIM technique was in good agreement with the chemical composition as supplied to us by ORNL. An analysis of the spatial distribution of the various alloying elements showed the existence of one large cluster consisting of three silicon atoms, two carbon atoms and two titanium (or possibly oxygen) atoms. It is highly improbable for such a cluster to form randomly for these rather low concentration alloying elements. This result indicates the existence of a positive binding enthalpy between carbon and silicon (and possibly titanium) in this LSIA alloy.

Research supported by the Energy Research and Development Administration.

The Range of a Focused Collision Replacement Sequence in Ordered Alloys

In a recent study of partially ordered Ni_3Mn irradiated with thermal neutrons Kirk et.al. claim to have developed a technique to measure the average length of a focused collision replacement sequence. These workers have measured the change in magnetic saturation with dose for different values of the long-range order-parameter (S). The change in magnetic saturation with dose was measured for S equal to approximately 0.79, 0.90 and 0.95. A quantitative computer analysis of the magnetic disorder produced by <111> focused collision replacement sequences showed that the magnetic disorder caused by a focused collision replacement sequence is a maximum at S=0.7 and decreases to zero at S=1. Kirk et al. calculated from their data an average sequence length of about 50 atoms along the <110> direction.

We are presently studying the random disordering produced by focused collision replacement sequences in Ni_4Mo by direct observation in the FIM. The ideas pertinent to the experiment are as follows. If one starts with a fully ordered alloy (S=1) then the FIM image of this alloy resembles that of a pure metal. The result of the lattice disorder produced by the focused replacement sequences is to change the image contrast to that which is characteristic of a random alloy. A specimen of the fully ordered alloys is irradiated in-situ with low energy neon ions (<1000eV) so that all the vacancies are left at the irradiated surface and the interstitials are driven into the bulk of the FIM specimen by the focused collision replacement sequence mechanism. After the irradiation the specimen is pulse field evaporated and the measured width of the disordered region (as detected by its random appearance) is used as a measure of the range of the focused collision replacement sequence.

During the past year much of the experimental effort had been expended on the preparation of ordered alloys of both Ni_3Mn and Ni_4Mo. The alloy Ni_3Mn proved to be a particularly difficult alloy to order because of the low temperature (400°C) at which the order parameter is equal to unity. Hence, we switched to the alloy Ni_4Mo for the following two reasons: (1) It achieves a long-range order-parameter of unity with a large domain size in relatively short times (a few hours); and (2) it is possible to obtain high quality FIM images of this structure fairly readily. Thus

the main progress in this area has been the production of ordered alloys of Ni_4Mo and the imaging of these specimens. Several preliminary irradiation experiments have been performed and the initial indications are positive. It is noted that this technique is applicable to a large number of ordered alloys which are imagable by the FIM technique (e.g. Ni_3Fe and Ni_3Al).

Research supported by the Energy Research and Development Administration.

The Interaction of Self-Interstitial Atoms with Impurity Gas Solute Atoms in Refractory Metals

This problem involves the preparation of alloys of refractory metals and the in-situ irradiation of the specimens with low energy (~1000eV) xenon ions. At less than 1000eV the main mechanism for self-interstitial production will be via the focused replacement collision sequence mechanism. The alloy specimens are irradiated in-situ at a temperature which is above substage I_E so that the SIAs produced are mobile. The SIAs then migrate towards both the sinks and the solute atoms and in the process clusters of complexes are formed. We are trying to study both the SIA-solute atom clusters and also any self-clusters that form. Towards this end we have constructed a quenching system to dope specimens with various gas atoms. Our initial efforts have centered on the Group VB metal tantalum, as this metal has a high solubility for a number of gases (e.g., O_2, H_2, and N_2) and is also readily imaged by the FIM technique. During the past year the quenching system has been operational for introducing gases into metals system. In addition, we have prepared FIM specimens of Ta and found it to be readily imagable It is expected that Ta-(N) specimens will, in the near future, be irradiated in-situ in the atom-probe FIM.

Research supported by the Energy Research and Development Administration.

The Study of Metallic Glasses by Atom-Probe Field-Ion Microscopy

A metallic glass, known commercially as Metglas 2826, with a nominal composition of 40at.% Fe, 40at.% Ni, 14at.% P and 6ay.% B was examined by the atom probe technique. The experiments were performed to establish the feasibility of studying the clustering behavior of the phosphorous and boron in this alloy. The clustering of phosphorous had been suggested as a possible mechanism for the embrittlement of this alloy following heat treatment below its crystallization temperature. Prior to the atom probe examination the specimen was annealed at 150 to 170°C for ~6h (a standard UHV bake out of the FIM).

The m/n spectrum for Metglas 2826 showed that the various constituents can be easily identified and resolved. The average composition was determined by the atom-probe technique and the spatial distribution of B and P was simultaneously determined. A statistical analysis of this data shows no obvious evidence for the clustering of the B and P. Thus our results indicate that 150 to 170°C is not high enough for any clustering to occur or that the kinetics of clustering is very slow in this temperature range. Future experiments on specimens neated to higher temperatures should readily determine at what annealing temperature detectable clustering begins as the crystallization temperature is approached from below.

The Metglas 2826 data were recorded in the presence of 10^{-7}Torr Ne, with a background pressure of 2.5×10^{-9}Torr, and at a tip temperature of 63K. The voltage range (V_{dc}) was varied between 18,500 to 19,000 V, the value of voltage fraction was 0.20 and the calibration parameters were; (1) pulse factor (α)-1.5; (2) total delay time (t_o)=56 μsec; and (3) flight distance (d)= 2231 mm.

Research supported by the National Science Foundation and the Materials Science Center.

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PHASE TRANSITIONS (AND LOW TEMPERATURE PHYSICS) STUDY GROUP

The widespread collaboration between members of the former Study Groups on Phase Transitions and Low Temperature Physics has demonstrated that there is little advantage in maintaining two distinct groups. Accordingly, they have been merged.

The research program of the Group covers a broad range of theoretical and experimental topics, which, from the present perspective fall roughly into five broad and somewhat interrelated fields of research: the critical point; the interface in multi-phase systems; liquid and solid helium; lattice phase transitions; and non-equilibrium processes in superconductors. The main area of study within each field are as follows:

1. Critical Point Studies

   a. Application of renormalization group methods to magnetic phase transitions, tricritical points, and the liquid-vapor critical point. (M. E. Fisher)

   b. Theoretical and experimental studies of tricritial phenomena in classical multicomponent liquid mixtures. (B. Widom)

   c. Finite size effects on critical phenomena. (M. E. Fisher, J. D. Reppy, R. Buhrman)

   d. Theoretical studies of the A-, A_1-, and B- transitions in superfluid ^{3}He. (N. D. Mermin)

2. Structure of the Interface in Multi-Phase Systems

   a. Structure, tension, and critical behavior of interfacial surfaces in liquids and multicomponent liquid mixtures. (B. Widom, W. W. Webb, G. V. Chester)

   b. Superfluid-normal fluid interface in the tricritical region of ^{3}He-^{4}He mixtures. (W. W. Webb)

   c. Development of a theory of surface free energies. (M. E. Fisher)

   d. Two-dimensional bilayers. (W. W. Webb)

3. Liquid and Solid Helium

   a. Nature of the magnetically ordered state of ^{3}He. (R. C. Richardson, J. W. Wilkins)

   b. The superfluid phases of liquid ^{3}He (D. M. Lee, J. D. Reppy, R. C. Richardson, V. Ambegaokar, N. D. Mermin)

   c. Superfluidity in restricted geometries. (J. D. Reppy, G. V. Chester)

4. Lattice Phase Transitions

   a. Studies of the displacive transition in titanium and zirconium body centered cubic alloys. (S. L. Sass)

   b. Theoretical studies of displacive lattice transitions. (J. A. Krumhansl)

   c. Computer simulation studies of melting and freezing in two and three dimensional systems. (G. V. Chester)

5. Non-Equilibrium Processes in Superconductors (V. Ambegaokar, R. Buhrman)

Phase Transitions (and Low Temperature Physics) Study Group Membership

V. Ambegaokar, Department of Physics
R. A. Buhrman, Applied and Engineering Physics
(for report see New Solid State Materials Study Group)
G. V. Chester, Department of Physics
M. E. Fisher, Department of Chemistry
J. A. Krumhansl, Department of Physics
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D. M. Lee, Department of Physics
N. D. Mermin, Department of Physics
J. D. Reppy, Department of Physics
R. C. Richardson, Department of Physics
S. L. Sass, Materials Science and Engineering
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W. W. Webb, Applied and Engineering Physics
B. Widom, Department of Chemistry
J. W. Wilkins, Department of Physics

V. AMBEGAOKAR, Professor, Department of Physics

Postdoctoral Associates:

P. Bhattacharyya

Research Assistants:

M. Levy

Low Temperature Properties of ^{3}He - I

A study of thermodynamics and transport properties in the superfluid phases of liquid ^{3}He.

Research supported by the National Science Foundation and the Materials Science Center.

Kinetic Theory of Superconductivity - II

Recently a study has been made of non-equilibrium properties of superconductors including photon a d phonon induced superconductivity.

Research supported by the National Science Foundation and Materials Science Center.

HIGHLIGHTS

a) Work by Rainer and Serene, started under this program, in which deviations from Bardeen-Cooper-Schrieffer pairing theory are expressed in terms of the scattering amplitudes of quasi-particles at the Fermi surface, thus providing insight into the strongly-coupled nature of the pairing in superfluid liquid ^{3}He, has recently been published.

b) Ambegaokar and Levy have completed a quantitative study of the way in which dissipation affects the hydrodynamic spin oscillations in the A-phase of superfluid liquid ^{3}He.

c) Bhattacharyya, working with C. Pethick and H. Smith in Copenhagen, has studied the weak damping of collisionless sound using a kinetic equation. Using methods they have developed for exact solutions of the kinetic equation near T_c, they have obtained a consistency condition from the difference between the damping of collisionless sound in the normal and superfluid states and the normal state viscosity.

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"Dissipative Effects in the Longitudinal Magnetic Oscillations of Superfluid Liquid ^{3}He-A", V. Ambegaokar and Miguel Levy, MSC Report 2479 (1975). See; Phys. Rev. 13, 1967 (1976).

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G. V. CHESTER, Professor, Department of Physics

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M. V. Rao

Research Assistants:

D. Ceperley
R. Gann
M. Kalos
J. Mon
R. Peterson

The work of Mr. J. Mon was carried out collaboration with Professor N. W. Ashcroft.

The Interionic Potential in Liquid Metals

We have successfully shown that details in the measured structure factors of many liquid metals can be accounted for by introducing polarization forces arising from polarizable d-shells of the ions. Liquid metals with strongly polarizable d-shells show a pronounced shoulder in the structure factor on the high wave number side of the first-peak. The appearance of this shoulder correlated extremely well with the presence of a polarizable d-shell of electrons on the ions. This shell gives rise to fluctuating dipole forces which in turn give rise to an enhanced interaction between the ions.

A qualitative calculation shows that the enhanced interaction leads to a non monotonic interaction which in turn leads to the observed shoulders in the structure factor. A more precise calculation is underway allowing for dynamic screening by the background electrons. We have successfully simulated shoulders on the structure factor for several model potentials. More simulation will be carried out to establish these results more precisely.

As far as we are aware this is the first time that a definite link has been demonstrated between the ion-ion interactions in liquid metals and the detailed form of the structure factor. We hope to learn more about these interactions by further accurate simulations and comparison with experimental structure factors.

Research supported by the National Science Foundation and the Materials Science Center.

The Equation of State of Metallic Hydrogen

Does metallic hydrogen exist in both fluid and crystalline phases — and if it does at what density does it crystallize?

We hope to answer both of these questions by carrying out accurate variational calculations—using Monte-Carlo simulation techniques.

At present we have obtained reasonably good energies in the liquid phase, using the best proton-proton interaction with an accurate screening function. This work is fairly laborious as it requires a several parameter search of a wide class of wave function.

Research supported by the National Science Foundation and the Materials Science Center.

Criteria for Melting and Freezing

Mr. Peterson has obtained the first complete set of Lindeman ratios (the ratio of the root mean square displacement of an atom to the lattice spacing) for the inverse power potentials (r^{-n}, for n= 1,4,6,9,12). These we obtained at the published melting densities and for values of the density in the neighborhood of the melting density.

A systematic trend was observed, the Lindeman number being 0.16 for the Coulomb potential and 0.13 for hard spheres. The ratio is very sensitive to variations above and below the melting values. A one percent change in density can produce a 10 per cent change in the Lindeman ratio.

We have thus established that the ratio varies slowly with the change in potential but rapidly in the neighborhood of melting. These systematic trends seem worthwhile investigating by examining the microscopic motions of the atoms at melting or reacting. The best approach to this is probably to use computer graphics. Dr. Greenberg has available programs which will allow us to do this.

The uncompleted portion of Mr. Peterson's thesis consists of determining the height of the structure factor S(K) on and near the freezing line. It is believed, that S(K) at the first peak is always close to 2.85 at freezing. Our major effort will be to determine how sensitive the peak height is to variations in the neighborhood of the freezing line.

Again if the "law" turns out to be accurate we will attempt to look at the microscopic correlations in an effort to understand it.

Research supported by the National Science Foundation and the Materials Science Center.

The Crystallization of Particles Interacting via "Unusual" Potentials

This work is concerned with systems of particles interacting via r^{-2}, r^{-3} and Yukawa potentials. Our aim is to study the crystallization and melting of these systems. When this has been completed we will have a complete picture of the crystallization and melting of all the inverse power potentials and also on a soft short range potential, namely the Yukawa potential: We should also extend some of this work to two-dimensions to see what insights can be gained. Corresponding work on quantum systems has been carried at New York University in collaboration with Professor Kalos – it is mentioned briefly below.

Mr. Gass has now established the approximate shape of the solid-fluid phase boundary for the classical Yukawa system. An accurate determination should be completed in a month or so. The necessary specialized programming for the r^{-2} and r^{-3} potentials has been completed; when the phase boundaries for these potentials have been determined Lindeman's ratio at melting will be calculated from our simulations and the height of the structure factor at freezing will also be determined. It will be of considerable interest to see if they fall accurately into the already established trend for these quantities.

The work reported below is an important part of my overall program – it does however receive much less support from MSC than the Cornell work. It is all carried out collaboration with Professor M. Kalos at NYU. Working in conjunction with him last year were Dr. M. V. Rao and Mr. David Ceperley.

Mr. Ceperley conducted extensive simulations of both Boson and Fermion systems at absolute zero. These were complementary to our classical studies of systems interacting via Yukawa potentials. He discovered that only a certain class of Yukawa potentials give rise to crystallization. We thus have for the first time an example of an interacting system which does not crystallize at absolute zero at any density. This result is true for both Bosons and Fermions.

Of particular interest is the fact that Mr. Ceperley was able to develop a useful technique that allows accurrate Monte Carlo calculations to be performed on systems with antisymmetrical ground states. This is an extremely important technical advance which we hope to exploit for a number of other systems.

Some other physical effects are worth mentioning. The crystals obtained by simulation were remarkable in that for both Fermi and Bose statistics they contained about 1 per cent of vacancies. In addition the Bose crystal had a Bose condensate of a few per cent near melting. Finally the crystals also showed the phenomena of pressure melting. That is to say, if the density is increased sufficiently the kinetic energy increases so fast that it easily overwhelms the potential energy and the crystal melts. The Yukawa potential thus provides a second example of pressure melting — the first example being the Coulomb potentials.

Dr. M. V. Rao has been working on a simulation of a classical liquid-vapor interface. Two important results have emerged. First he has shown that a much longer time must be allowed for the simulation of the interface before equilibrium is reached as compared with bulk simulations. With a very long simulation he was able to demonstrate that he had reached equilibrium with a uniform temperature and pressure. Second in the equilibrium state the surface layer of the fluid has a 'patchy' structure in which patches of liquid density fluid form, dissolve and reform in a region in which the remaining atoms appear to form a very long density vapor. The long time average is observed in a straightforward simulation. However the patches persist for physically interesting times and may have important consequences.

Research supported by the National Science Foundation, the Energy Research and Development Administration and the Materials Science Center.

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Postdoctoral Associates:

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Theory of Phase Transitions, Critical and Multicritical Phenomena

Scaling Functions for Crossover and Multicritical Behavior

Statistical Mechanics of Inhomogeneous and Finite Systems

Mathematical Foundations of Statistical Mechanics

The theoretical programs include:

(a) The application of renormalization group techniques to elucidate the nature of multicritical phenomena, especially the full characterization of bicritical and tricritical behavior in magnetic and fluid systems.

(b) The calculation of the basic scaling functions which describe behavior in the vicinity of a critical point subjected to various perturbations which change the nature of the critical singularities. This encompasses: (i) renormalization group calculations of crossover scaling functions for multicritical points; (ii) calculations by series expansion and extrapolation techniques of these scaling functions; (iii) exact mathematical calculations for crossover in finite Ising models, including boundary condition effects.

(c) Studies, by exact analytic methods, of the influence of spatially regular inhomogeneities (such as frozen-in vacancies, or impurities) on specific heat singularities;

(d) Rigorous statistical mechanical formulation of the existence and basic properties of the free energy of a system, especially as regards surface and boundary free energies.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

A significant study completed during the year, in collaboration with Au-Yang, was the exact calculation of the critical temperature shift induced in a two-dimensional Ising ferromagnet by a finite concentration of point impurities distributed on a regular $m \times n$ grid. Various types of impurities including missing spins, missing bonds, and missing bond pairs have been handled exactly. The results depend nonanalytically on the concentration, x, in the form

$$T_c(c)/T_c(0) = 1-Q_1x+Q_2x^2\ln x-Q_3(n/m)x^2-Q_4x^4\ln^2 x+\ldots .$$

It is especially noteworthy in relation to the theory of randomly distributed point defects, that the coefficients Q_1, Q_2, and Q_4 are "universal" to the extent that they are independent of the ratio n/m. (Only Q_3 depends on this "shape ratio".) In addition, Au-Yang found how the amplitude $A(x)$

of the logarithmic specific heat singularity varies nonanalytically with x. This result and the T_c-shift can be understood in terms of a more general scaling theory that should be applicable also in three-dimensions and to more complex systems.

The previous years technical breakthrough by Nelson, allowing the calculation of crossover scaling functions for multicritical phenomena by ε-expansion renormalization group methods, has been exploited for a variety of problems. Foremost amongst these applications has been a study, still continuing, of the crossover scaling functions for bicritical points, such as typified by the spin flop point in antiferromagnets. The first calculations were restricted to the high temperature or disordered half of the phase diagram (in the temperature-anisotropy plane). The results, to leading order in $\varepsilon = 4-d$ (where d is the spatial dimensionality), where very informative and in most encouraging numerical agreement with the direct three-dimensional calculations of Gerber based on series expansions for the classical Heisenberg-XY- Ising models. Further renormalization group work by Domany and Nelson has yielded the scaling functions in the first region below the critical line (away from the "flop" phase boundary) which is a domain so far completely inaccessible to series expansion techniques. Experiments underway on MnF_2, $GdAlO_3$, and other antiferromagnets should yield data for comparison with these theoretical results.

An important feature of the renormalization group calculational techniques is the ability to study in detail the effects of various small symmetry breaking terms which are always present in real magnetic materials arising e.g., from lattice potentials. In many regions of the phase diagram such terms have negligible effects: technically they are "irrelevant". However, in studies with Nelson and Mukamel it has been shown how these interaction terms can become "dangerous" in certain regions, in particular, near the ordered phase transitions: the nature of the equation of state changes significantly. This phenomena is being studied in detail for perturbations of cubic symmetry both in the context of the spin flop transition and in systems which are otherwise isotropic in spin space.

A relatively simple but informative application of scaling theory, with Z. Rácz of Budapest, has been made to the theory of the critical behavior of the nonlinear relaxation time of a system. It had been believed that the linear (response to an infinitesimal displacement) and nonlinear relaxation times would diverge in the same way as T approaches T_c i.e., with equal critical exponents $\Delta^{(\ell)}$ and $\Delta^{(n\ell)}$. However, this is incorrect; instead the general relation is $\Delta^{(n\ell)} = \Delta^{(\ell)} - \beta$, where β is the exponent for the order parameter. Experiments on alloys (using neutron diffraction) and numerical studies of model systems bear out this conclusion.

Studies have also been underway, with Springgate, of a novel method of approximating functions of two variables on the basis of their power series expansions. The method, distinct from the Canterbury and related two-variable Padé approximants, holds promise of being especially fruitful near singularities of multicritical type; but this must be tested in practical trials now underway.

Distinct progress has been made, with Caginalp, in defining and proving the existence of surface or boundary free energies in Ising spin systems with ferromagnetic interactions. The proofs constructed are the first rigorous general results of this type.

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D. M. LEE, Professor, Department of Physics

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W. J. Gully

Research on the properties of superfluid ^{3}He has continued during the past year. The nuclear magnetic properties of both the A and B phase of this superfluid have been investigated by continuous wave (CW) and pulsed nuclear magnetic resonance (NMR) techniques. Millidegree temperatures have been achieved by Pomeranchuk cooling with the ^{3}He sample either contained directly in the compression cell or in an auxiliary cell thermally connected to the compression cell. This latter method (indirect Pomeranchuk cooling) has the advantage of permitting study over a wide pressure range below melting pressure in arbitrary magnetic fields.

CW NMR Measurements

Satellite NMR lines in the A phase have been observed by CW techniques in both the longitudinal and transverse resonance configurations in a compression cell. The longitudinal satellite frequency Ω_{sat} was related to the main longitudinal frequency Ω_{main} by the ratio $R_L(T)=\Omega_{sat}(T)/\Omega_{main}(T)$, where $R_L(T)$ was found to be a weak function of temperature varying between .67 and .74 over the whole temperature range corresponding to ^{3}He A along the melting curve. The transverse satellite frequency $\omega_{t.s.}$ was found to obey the relation $\omega^2_{t.s.}-\omega^2_0 = \Omega^2_{t.s.}(T)$ where ω_0 is the Larmor frequency and $\Omega_{t.s.}(T)$ is a function of temperature only. The ratio R_T of $\Omega_{t.s.}(T)$ to the main longitudinal frequency $\Omega_{main}(T)$ was found to be constant over the A phase with a value $R(T) = \Omega_{t.s.}(T)/\Omega_{main}(T) = .835$.

The behavior of these satellite lines was investigated for various geometries, radio-frequency power levels, applied magnetic fields and compression rates. It was concluded that the satellite lines were probably produced by texture effects which could be greatly enhanced by superflow. Structures such as solitons have been proposed as a possible explanation of the satellites.

Pulse NMR

Pulsed NMR measurements have been performed in a parallel plate geometry in both the A and B phases of superfluid ^{3}He at pressures of 18.7 and 27 bar. The sample cell was cooled by a separate Pomeranchuk cell using the technique of indirect Pomeranchuk cooling. The frequency of the free induction decay signal following tipping pulses of varying angle Θ was determined in both superfluid phases. The results in the A phase were in agreement with the theory of Brinkman and Smith. In the B phase, the frequency began shifting away from the Larmor frequency at $\Theta \cong 104°$ as predicted by Brinkman and Smith but the frequency shift vs. Θ curve fell well below that computed by Brinkman and Smith. The above results are similar to those found by Osheroff and Corruccini at melting pressure. After a large tipping pulse, the frequency tended to recover smoothly to the Larmor frequency in a time of about 1 msec. Preliminary measurements of other interesting transient effects have been made by pulsed NMR techniques during the 1975-1976 period.

Research supported by the National Science Foundation and the Materials Science Center.

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Superfluid Liquid Helium-3

After concluding the analysis of f-wave models of the A_1 phase, attention was shifted to the problem of constructing a proper hydrodynamic description of the A-phase. Attempts at such a hydrodynamics in the literature start with the assumption that the vector $\underline{l}$ specifying the orbital symmetry axis of the Cooper pair is spatially uniform. When this is the case it is possible to define a phase variable, whose gradient is the superfluid velocity $\underline{v}_s$, in close analogy to the procedure followed in theories of superfluid helium-4. When $\underline{l}$ is not spatially uniform, however, a phase cannot be defined. It is important to consider this case both because the boundary condition developed earlier by Ambegaokar, de Gennes, and Rainer virtually insures that $\underline{l}$ can never be uniform, and because a uniform $\underline{l}$ obscures one of the essential distinguishing features of the A-phase: the intricate relation between pair angular momentum and superfluid flow.

We developed a generalization of the superfluid velocity valid for general configurations of $\underline{l}$. The peculiar nature of ^{3}He-A emerges in an equation (the analogue of the London equation in a superconductor) which specified the (non-zero) value of the curl of $\underline{v}_s$ as a linear combination of gradients of $\underline{l}$. This relation has a simple geometrical interpretation near surfaces, and should form the foundation of subsequent discussions of flow patterns in ^{3}He-A. A first application led to the remarkable concluson that the equilibrium configuration of ^{3}He-A in various geometries of cylindrical symmetry, is very likely to have a non-vanishing orbital angular momentum.

Efforts were also begun to develop a proper non-linear hydrodynamics incorporating the condition on curl $\underline{v}_s$.

Research supported by the National Science Foundation and the Materials Science Center.

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Introduction

The main interest of the group lies in the area of phase transitions and superfluidity. During the past year a technique has been developed which permits the measurement of the superfluid density both for superfluid ^{3}He and for thin films of ^{4}He adsorbed on a suitable substrate.

Superfluid and Phase Transition Studies with ^{4}He

In the ^{4}He superfluid work the emphasis has been on the study of the properties of thin adsorbed films and helium contained in narrow (60Å) channels. At present a fairly clear picture has emerged on the question of the influence of these restricted geometries on the excitations of the helium system. It has been shown in this laboratory and elsewhere that the dominate phonons at low temperature reflect the nature of the restricted geometry. That is we find one-dimensional phonons dominating for helium contained in narrow channels such as the pores of Vycor glass while adsorbed helium films display a two-dimensional aspect for films plated on a flat surface.

Our main interest has now turned to the nature of the superfluid transition in such restricted geometry systems. Fourth sound measurements, published last year (Kiewiet, Hall and Reppy PRL 35, 1286 (1975)), had shown the surprising result that the ^{4}He-Vycor system exhibits a sharp superfluid transition despite the highly confined geometry of the Vycor pores. Furthermore, the superfluid density approaches zero at the transition with the same "two thirds" power-law as seen in unconfined bulk helium.

It is known that the channels in porous Vycor glass form a highly interconnected three dimensional net. It may be that this essentially three dimensional or bulk behavior for the superfluid density near the transition is a consequence of the topology of the channels. If this is the case, then we are dealing with a very promising system for investigating the influence of geometry on the nature of phase transitions since it would be feasible to change the geometry in a known fashion. We have now started on a program to investigate this possibility.

A simple prediction that one can make on the basis of the full pore fourth sound measurements and the idea that the topology controls the critical behavior of the superfluid is that a helium film would be expected to display the same two thirds power-law dependence near the transition since the basic topology of the substrate is the same for the film as for the full-pore case. Using an adaptation of Andronikashvilli's torsional oscillator method for measuring ^{4}He superfluid density, we have been able to confirm this prediction. Except for a renormalized transition temperature, depending on film thickness, the superfluid density in the film displays the same power-law as bulk helium. We expect to publish these results in the near future.

The next step in this investigation is clear, one should change the topology. The plan then is to look at the temperature dependence of the superfluid density in a two dimensional system. The oscillators which we have developed for these measurements permit a resolution of the superfluid density with a precision of better than 10^{-3} even for the projected design for the two dimensional measurement. In addition, we also plan to investigate the influece of various noble gas preplatings on the low temperature excitations of the helium system. One graduate student, David Bishop, and a postdoc, Joseph Berthold are mainly engaged in this work.

Research supported by the National Science Foundation and the Materials Science Center.

^{3}He Experimental Program

The ^{3}He research effort is carried on in close collaboration with the two other faculty members of the Cornell Low Temperature Group, D. M. Lee and R. C. Richardson and their students and postdocs. In an attempt to make my contributions not only collaborative but complementary, the efforts of my group have concentrated on hydrodynamic measurements in the superfluid phases of liquid ^{3}He. In this work we have been using somewhat similar techniques for both the ^{4}He and ^{3}He work.

Recently we have completed a measurement of the superfluid density of liquid ^{3}He for both the anisotropic A phase and the isotropic B phase. By controlling the texture of the anisotropic phase through the use of an externally applied magnetic field, we have been able to make the first measurements which definitely demonstrate the tensor nature of ^{3}He-A. The experimental technique is based on the Andronikashvilli method using a small but high Q (about 10^5) torsional oscillator similar in concept to those used for the ^{4}He superfluid density measurements. A letter has been submitted to PRL on these measurements.

In addition to the superfluid results mentioned above which are in accord with theoretical expectation, we have also obtained information on the temperature dependence of the viscosity for the superfluid phases. These measurements are of considerably higher precision than earlier work but in contrast to the superfluid density results are at variance with the present theoretical estimates for the temperature dependence near the transition temperature. We wish to check these measurements with a different apparatus before submitting them for publication.

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Studies of Superfluid ^{3}He

Since the discovery of the superfluid phase of liquid ^{3}He in our laboratory in 1972 our research program has been directed toward investigating some of the unique properties of this unusual fluid. Although there are several distinct superfluid phases, the microscopic structure of each modification is similar to that of superconductors with BCS pairing of the ^{3}He atoms. In ^{3}He however, the pairs form with their spins in a triplet magnetic state and have a net odd angular momentum. As a consequence of the odd angular momentum the superfluid has spatial anisotropies. Moreover, since ^{3}He atoms have no charge, there is no Meissner effect shielding the fluid from magnetic fields. Thus, various magnetic probes may be used for making a microscopic observation of the arrangement of the fluid. Our present direction of research is the examination of the singularities, textures, and superfluid anisotropies that arise as a consequence of the odd angular momentum of the pairing.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

During the past year a major part of our effort has been devoted to updating our cryogenic facilities in order to be able to perform the superfluid ^{3}He studies in a well controlled environment. The cryostat in our shielded room has been converted from a compressional cooling apparatus to a nuclear demagnetization cryostat. The compressional method is quite effective for many studies of the fluid at the melting pressure but the coexistence of the solid in varying uncontrolled fractions makes the preparation of homogeneous superfluid states difficult. Our first step in improving the millidegree facility was to recondition our dilution refrigerator that provides the critical first cooling stage. The refrigerator is now capable of running continuously at 8mK rather than the previous minimum of 14mK. This represents a significant improvement of the initial conditions of the magnetic cooling cycle. The entire nuclear cooling stage has been completed and is under test. Initial studies with the new cooling facility will include measurements of the mobility of ions, measurements of the superfluid viscosity, and magnetic studies of the superfluid domains.

In collaboration with David Lee and his students we have also measured the spectroscopic details of the transverse and longitudinal magnetic spectra of the superfluid A phase. A surprising recent feature of these studies has been the appearance of unpredicted satellite lines, currently thought to be magnetic "singularities" of the superfluid phase.

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Critical and Cooperative Phenomena

Understanding the behavior of interfaces between fluid phases in near critical condition continued to attract our attention as the problem continued to unfold cases of new physical interest. Studies of interfacial waves on the near-critical interface between the normal fluid and superfluid in isotopic mixtures of ^{3}He and ^{4}He were finally initiated near the end of this period using the special apparatus that we had developed for this experiment and most recently used for quasi-elastic light scattering measurements of critical slowing down near the tricritical point in this system as reported last year.

A preliminary analysis of possible methods for detecting the concentration profile in the interfaces that develop between three coexisting fluid phases in quaternary, near critical mixtures was carried out to assess feasibility. It was determined that ellipsometric techniques have a high probability of working and plans were developed in response to a proposal by Professor Ben Widom to collaborate on these experiments in quaternary liquid mixtures.

Research supported by the National Science Foundation and the Materials Science Center.

Biophysics

In continuing collaboration with Professor E. L. Elson we are applying fluctuation correlation analysis to biophysical problems. Measurements of diffusion in lipid bilayers and smectic liquid crystals composed of materials of biological interest have revealed the need for fundamental physical studies in these systems – independent of the biophysical problems. However, exploratory experiments on the mobility of membrane components in mammalian cells in culture under situations of particular biological interest has received most of our attention during this period. Our techniques, providing a unique capability for this program, have evolved from methods we originally developed for physical studies of fluctuations in condensed matter. Experiments on the cooperative kinetics of CO binding to hemoglobin continue.

Research supported by the National Institute of Health and the National Science Foundation.

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Phase Transitions and Critical Phenomena

The goal of this research is to determine and to understand the quantitative aspects of phase transitions and of the critical points of phase equilibria. Currently, the emphasis is on a three-phase equilibria and their tricritical points in multicomponent liquids, and on the properties of the interfaces in such phase equilibria. The research is both theoretical and experimental.

Models of Chemical Reaction Kinetics

The goals of the research are to determine the range of validity of the linear and non-linear phenomenological equations of chemical reaction kinetics, and to study the connection between the rate constants that appear in the phenomenological equations, and the cross sections and transition probabilities of the microscopic processes that underlie the chemical reaction.

These research projects supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

The three interfacial tensions $\sigma_{\alpha\beta}$, $\sigma_{\beta\gamma}$, and $\sigma_{\alpha\gamma}$ in the three-liquid-phase (α,β,γ) quaternary system benzene-ethanol-water-ammonium sulfate, were measured at 21°. The condition of spreading, $\sigma_{\alpha\gamma}=\sigma_{\alpha\beta}+\sigma_{\beta\gamma}$, was found to hold to within the precision of the measurements (±4%) through the whole of the three-phase region from one critical end point to the other. This verified the earlier theoretical prediction that sufficiently close to a tricritical point (21° is only 9% below the tricritical-point temperature on a scale of absolute temperatures), where the phase transitions are known to be describable with a single order parameter, the highest of three interfacial tensions will be the sum of the two lower. The variation of $\sigma_{\alpha\beta}$ with $\sigma_{\beta\gamma}$ through the three-phase region at fixed temperature was calculated from the van der Waals, Cahn-Hilliard theory, using Griffiths' form of the free energy. The measured values at 21° were found to be in good qualitative accord with that theoretical result, too.

On the chemical-reaction kinetics project, a simple one-dimensional model of a dissociation recombination reaction $M + A_2 \rightleftarrows M+2A$ was found, in which the collision dynamics could be treated by exact analytical calculation and the statistical aspects could be determined by highly accurate numerical solution of the associated non-linear master equation. The results make doubtful the popular ascription of a "negative activation energy" for recombination to a failure of an equilibrium approximation.

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X-Ray Synchrotron Radiation and Electronic Excitations in Metals

The last year has mostly been spent developing equipment and expertise for using 2-100 keV x-rays from the Cornell 12GeV Electron Synchrotron in experiments on condensed systems. (See B. Batterman's report for details on this aspect.) In addition it has been possible to complete one experiment: a measurement of systematic structure in the K-edge absorption spectra of the 4d transition metals (Y, Zr, Nb, Mo, Ru, Rh, Pd, and Ag). There is considerable structure on or about the edge (up to 150eV). Systematics in the feature closest to the edge are attributed to structure in the "local-band-structure" density of states. If this interpretation is correct, then work in two different directions is appropriate. On the experimental side L-absorption spectral should reveal enhanced structure owing to both the narrower core-hold width and the increased transition rate (atom p, instead of s, to d band). Preparations for such experiments are underway. Theoretically the first task is to extend band-structure calculations to higher energy (at least 50-100 eV above the Fermi level) and to produce density of states separated into different angular momentum final states. A start has been made on this project using the fast band-structure-calculation procedures of O.K. Andersen. Eventually it should be possible both to calculate matrix elements and to extend the scheme to calculate the extended absorption (and fluorescence) fine structure.

Work on electronic excitations has also continued along more conventional directions. In particular the work on 4f excitation energies in the rare earth metals has been extended to include relativistic effects within a crude self-consistent scheme. Within the assumption of a compeletely screened final state, in which the atomic site having the 4f hole is electrically neutral, 4f binding energies are estimated which are in even better agreement with experiment than our previous non-relativistic calculation. Further if we require the atomic site after 4f photo-ejection to be charged, then the 4f binding energies are increased by 4-6eV, thus strongly suggesting that the 4f photoemission event corresponds closely to one where the 4f hole is completely screened (within the atomic cell). Another continuing concern is the relative placement of the Fermi level with respect to the electrostatic potential at the edge of the Wigner-Seitz sphere, i.e., the internal work function (IWF). In Ni we have the IWF for two quite different potentials: one where the exchange-correlation hole is localized at the center of the atomic cell and the other where the hole roughly follows the electron. The first potential, more attractive than the second, has an IWF nearly 5eV lower. When combined with the measured work function, the two calculations imply a surface dipole energy of -.4eV and 4.5eV, respectively. Both results are ridiculous and suggest, along with similar evidence in other metals, that we are a long way from understanding the relative placement of energy levels in metals. This problem becomes even more severe when we consider the spectroscopy of absorbed or implanted atoms, a subject that we are continuing to study.

Research supported by the National Science Foundation and the Materials Science Center.

Dilute Magnetic Alloys

The numerical renormalization-group techniques due to Wilson have been extended to consider the Anderson model for the formation of local moments in a metal. For the symmetric Anderson model the temperature-dependent susceptibility can be calculated with an accuracy of a few per cent over the full, physically relevant range of the parameters of that model. The low-temperature susceptibility maps precisely into that for the spin-1/2 Kondo Hamiltonian. For the asymmetric Anderson model the mapping is onto the Kondo model plus potential scattering. Finally some progress has been made in calculating the transport problems. In particular we can see how the approximate Hamiltonian describing the low-temperature behavior, where the local moment is being compensated by the conduction electrons, can be used to calculate the electron relaxation time. Connection can be made with the heuristic approach of Noziéries for calculating properties at low temperatures. We are attempting to develop a scheme to calculate the electrical resistance over the full temperature range.

Research supported by the National Science Foundation.

Four-Particle Exchange in Solid ^{3}He

Work has continued on understanding the low temperature properties of bcc solid ^{3}He near the phase transition. We have already demonstrated that the delocalization of the ^{3}He atoms can lead, in addition to the well-known Heisenberg two-spin interaction, to a significant four-spin term in the Hamiltonian. A variational treatment of the free energy leads to a description of the entropy in term of the properties of a Heisenberg system with a temperature-dependent exchange interaction. The temperature dependence is driven by the four-spin term and yields, for reasonable values of the parameters, entropy curves which are similar to experiment. The extension of the approach to finite magnetic fields is considerably more difficult and is hindered by the poverty of experimental data.

Research supported by the National Science Foundation.

HIGHLIGHTS

I. Systematic structure on the K-edge absorption spectra of the 4d transition metals has been identified using synchrotron radiation from the Cornell 12GeV Electron Sychrotron.

II. Relativistic calculations of the 4f excitation energies in the rare earth metals are in striking agreement with the XPS measurements.

III. Considerable progress has been made in extending the Wilson renormalization group techniques to calculate properties of the Anderson model for dilute magnetic impurities.

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NEW SOLID STATE MATERIALS STUDY GROUP

This is one of the most rapidly developing of the Study Groups. The emphasis throughout is on materials which have not been previously prepared, and which are anticipated to have novel and perhaps useful properties; or upon known materials which have been "rediscovered" because of evolving technological interest, or because they exhibit interesting thermal or electric properties when examined in new regimes of temperature, microstructure, type of measurement, impurity control, etc. Novel and very careful preparation and characterization techniques are evident throughout.

Two program areas, one-dimensional materials and composite materials for photothermal selective surfaces, are the foci for highly interactive and cooperative efforts involving several faculty each. Other program areas include cooperative phenomena in anisotropic conducting compounds, electronic properties in intermetallic compounds, and lattice excitation spectra of amorphous materials.

New Solid State Materials Study Group Membership

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Multilayered Superconductors

We have prepared multilayered superconductors, consisting of alternating layers of Ge and Al and we have studied the superconducting properties of this system as a function of layer thickness. Briefly, the results are as follows: Thinly layered specimens ($d_{Al} \approx d_{Ge} = 30 \ldots 300$Å) have superconducting properties reminiscent of naturally layered superconductors intercalated with organic molecules in that $H_c^{\perp}$ vs. T plots show a positive curvature. $H_c^{\parallel}$ follows the standard prediction for thin films since both theory and experiment indicate that the layers are decoupled by the applied parallel field. Closer examination shows that the superconducting parameters vary somewhat discontinuously with layer thickness and exhibit jumps for $d \approx 80$Å and $d \approx 200$Å. Electrical resistivity measurements in the normal state indicate that the 80Å discontinuity is due to a break up of the Al film (island formation).

In addition to the above system we have studied multilayered superconductors consisting of alternating layers of Al and Pb_xIn_{1-x}. Investigation of the superconducting properties of these films show the presence of strong surface pinning. Presently we are investigating methods to eliminate surface pinning in order to study bulk pinning by the layered structure per se. Preliminary experiments are carried out to enhance bulk pinning through the use of thin (ca 50Å) Fe layers interspaced between λ separated Pb_xIn_{1-x} layers.

Structure of Amorphous As_xSe_{1-x}

This project has progressed slowly because the student was a full time Teaching Assistant during both terms. The intention of the investigation is to determine structural parameters of doped and undoped As_x-Se_{1-x} through careful viscosity measurements and the application of theories developed originally for organic polymers. The viscosity of both doped (As) and undoped As_xSe_{1-x} has been measured between 160 and 300°C. It is found that the viscosity of doped As_xSe_{1-x} lies below that of undoped As_xSe_{1-x}. In addition, there is evidence that the preparation condition of undoped As_xSe_{1-x} influence the viscosity. Samples quenched from high temperature show a slightly lower viscosity than those quenched from lower temperatures. Both effects can be understood in terms of decreasing chain (or sheet) dimensions. Presently, we are investigating the viscosity of evaporated thin films of As_xSe_{1-x}. It is expected that such films have lower viscosities than bulk quenched samples, but that anneals above T_g increase the viscosity close to that measured in bulk samples.

Fracture Toughness of Metallic Glasses

The fracture toughness and yield strength of Fe-Ni base metallic glasses have been studied as a function of the annealing treatment. It was found that the fracture toughness decreases much faster with increasing annealing than the yield strength. Electronmicroprobe analysis shows that the decrease in fracture toughness occurs at temperatures at which P becomes mobile. Phenomenologically, the embrittlement process in metallic glasses is similar to P grain boundary embrittlement in steels.

Polymers

In cooperation with Professor Kramer, double exposure holography is being used to measure the strain energy release rate of growing crazes in PS and PMMA.

Other Areas

In cooperation with Dr. Krakow at Xerox Research Laboratories, transmission electron microscopy is used to resolve the atomic structure of Au surfaces, specifically the 100 surface. The method is based on the fact that a thin film diffracts into forbidden reflections when the film thickness is a non-integral number of unit cells. It is expected that the method contributes to surface science, since it samples (unlike LEED) the first layer only and yields a direct image of the surface.

These research projects are supported by the National Science Foundation, the Air Force Office of Scientific Research, the Army Research Office and the Materials Science Center.

HIGHLIGHTS

a) For the first time, a man made multilayered material has been produced that exhibits superconducting features characteristic of naturally layered systems. If it can be confirmed that the mechanisms are similar in both cases, a much wider variety of layered materials than the present few naturally layered materials can be produced.

b) For the first time, transmission electron microscopy has been used to resolve the atomic structure of single surface layers. The method samples the first layer only and yields a direct image of atomic resolution of the surface.

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Metallic Microcrystal Research

A major effort in this area has been the study of the growth mechanisms and size distributions of ultra-fine metal particles. To account for the characteristic skewed size distribution that is consistently obtained with metal particles produced by inert gas evaporation a simple model for particle growth by coalescence has been developed. This model predicts a log-normal distribution function which closely fits the observed distribution functions both as obtained in our laboratory and as found in the literature for inert gas evaporation. The model has also been applied to other particle growth situations where coalescence is likely to occur. In general it has been found that where coalescence is probably the dominant growth mechanism a log normal distribution function (LNDF) occurs. It is postulated that a LNDF is a necessary, although not definitely sufficient, proof of coalescence growth. This viewpoint has been applied to supported metal catalysts where a LNDF is often found. It appears that coalescence may be a more common cause of catalyst ripening than is usually thought.

The width of size distributions of particles produced by various techniques has also been examined. In general the width of the distribution is found not to be a strong function of exact production conditions but to depend only on the type of process employed. In particular two-dimensional growth processes, such as occur in discontinuous film growth, consistently yield narrower distributions than do three-dimensional processes.

Research into quantum size effects of ultrafine metal particles has been continued. Infrared absorption measurements have been extended to aluminum particles with mean diameters <100Å. The experiments yield an infrared absorptivity whose frequency dependence is as expected but whose amplitude is several orders of magnitude greater than either the Gorkov-Eliashberg quantum theory or the classical theory. The size dependence of the absorptivity is also not as predicted. Experiments to account for this anomalous result are continuing.

Research supported by the National Science Foundation and the Materials Science Center.

Superconducting Sensors

The goals of this program are the development of a fundamental understanding of the sensitivity limits of superconducting quantum sensors and the development of improved, practical superconducting magnetometers and radiation devices.

During the past year considerable effort has been given to the continuation of our direct measurements of current-phase relations in superconducting weak links. The results of these measurements have now been correlated with both superconducting magnetometer response and with weak link I-V

characteristics. The experiments clearly indicate that the dc current-phase relation is a major determinant of device response. However relaxation phenomena also play an important role at high frequencies and voltages.

The analysis of rf magnetometer (SQUID) performance and noise limits has been extended to the case of the low critical current or so-called inductive mode of operation. The results show that for minimum intrinsic device noise the critical current of the SQUID weak link should be sufficiently small that the device is just inside the inductive regime. However until significant improvement in rf amplifiers is achieved the practical advantages that are obtained by operating in this regime are slight. The upper frequency limits of rf SQUID operation have also been explored. Not too surprisingly, the analysis reveals that for maximum performance a bias frequency equal to a slightly greater than the natural response frequency of the SQUID ring is most appropriate.

Finally a program to fabricate variable thickness microbridges of sub-micron dimensions using electron beam lithography has been initiated. Microbridges with all dimensions $\lesssim 0.3\mu$ have been fabricated between thick Nb electrodes with sputter etching techniques. Both Nb bridges and normal metal bridges have been produced. The performance of the Nb-N-Nb bridges look particularly promising at present.

Research supported by the Office of Naval Research and the Materials Science Center.

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Polymeric Phosphinates of Group VI Metals

As a prelude to the synthesis of a series of polymeric phosphinate derivatives of trivalent chromium, some of the divalent chromium analogs having the general formula $[Cr(R_2PO_2)_2L_x]_n$ were prepared in which L is a solvent molecule (tetrahydrofuran), x is either 0.5 or 0.0 and R is an organic group. Compounds of similar character were obtained from metathetical reactions of chromium (II) chloride and the potassium salts of diphenylphosphinic acid and methylphenylphosphinic acid. The magnetic properties of the air-sensitive, light-colored, polymeric solids were examined by Professor J. C. Scott. The effective magnetic moments at room temperature of 4.6 B.M. are consistent with high-spin octahedral Cr(II). From this and the stoichiometry it was concluded that some of the phosphinate oxygens occupy in edge bridging or face bridging positions. No evidence of crystallinity was obtained but the solubility of the methylphenylphospininate complex in common polar solvents augurs well for planned synthetic applications.

The Mo(II) analogs were prepared from the appropriate phosphinic acid and either hexacarbonyl molybdenum or molybdenum(II) acetate in diglyme. The former method gave the previously described insoluble, salmon-colored polymer $[Mo(Ph_2PO_2)_2]_n$. This product contained a small amount of an unidentified, air-sensitive metal carbonyl impurity and was shown by Scott to have an effective magnetic moment of 2.0 B.M. at room temperature. The acetate route gave a mixed-ligand polymeric species of the type $[Mo(O_2PPH_2)_x(CH_3CO_2)_{2-x}]_n$ (where x was approximately 1.75) indicative of incomplete substitution.

Complete substitution was obtained when a dithiodi(organo)phosphinic acid was employed in reactions with either the acetate or the chloride of divalent molybdenum. The resulting, diamagnetic complexes with the general formula $[R_2PS_2)_2Mo]_n$ (where R is either phenyl or ethyl) represent the firs examples of this type of complex. A single crystal structure determination is in progress (J. Lemley, MSC).

Research supported by the Materials Science Center.

Solid Phase Synthesis

The presence of significant quantities of by-products di-n-butyltin chloride and tri-n-butyl chloride in the attempted solid phase synthesis of the pentametallic oligomer, $[ClSnBu_2Os(CO)_4]_2SnBu$ (where Bu is n-butyl) prompted a detailed study of the initial phases of substitution of the polymer support. Macroreticular copolymers of styrene and divinylbenzene were functionalized with resin-bound analogs of phenylmercuric chloride, phenyllithium, and phenyldi-n-butyltin chloride at levels lower than 0.05 meq per gram of resin. Resino-phenylmercuric chloride was formed by the reaction of mercuric trifluoroacetate with the resin followed by trifluoroacetate--chloride exchange. Resino-phenyllithium was formed by the action of n-butyllithium on resinophenylmercuric chloride and also by direct lithiation using the tetramethylethylene-diamine complex of n-butyllithium. Resin-phenyllithium reacted with di-n-butyltin dichloride to form resino-phenyldi-n-butyltin chloride. In this case, relatively large quantities of resino-phenyltri-n-butyltin were also produced as a result of adsorbed n-butyllithi present on the reacting polymer. Upon cleavage with hydrogen chloride this and any doubly terminated organotin moieties produced by the by-products mentioned above. Degradation of the high resolution ge permeation chromotographic columns caused by the by-products has thus far severely limited the quantity of the pentametallic oligomer which can be separated.

Research supported by the Materials Science Center.

Mixed Metal Clusters. The Crystal and Molecular Structure of μ-Carbonyl-Bis-μ-(Tetracarbonylcobaltzinc)-Bis-(Tricarbonylcobalt)

In collaboration with Professor R. E. Hughes, M. E. Leonowicz and Dr. J. T. Lemley, the crystal and molecular structure of a novel mixed metal cluster compound, $Zn_2Co_4(CO)_{15}$, was determined by single crystal x-ray diffraction methods. The compound, prepared in an earlier study by S. E. Hayes, was shown to crystallize as discrete molecules which consist of two tricarbonylcobalt groups linked by a Co_i-Co_i bond 2.673(2)Å and bridged by a carbonyl group and two mirror-related zinc atoms. The Co_iZn bonds of 2.478(1) Å produce a Co_i-Zn-Co_i angle of 65.27° and the dihedral angle of 117.5 between the Co_i-Zn-Co_i bridges separates the zinc atoms by 3,568 Å. Each zinc bears a tetracarbonylcobalt group of approximately C_{3v} symmetry with an average C(axial)-Co_t-C(equatorial) angle of 98.2° and a Zn-Co_t distance of 2.352(1) Å. The three cobalt atoms bonded to each zinc are nearly coplanar with Co_t-Zn-Co_i angles of 147.16° and 146.75°. This is the first example of zinc incorporated in a transition metal cluster.

Research supported by the Materials Science Center.

Synthetic Intermediate for Metal-Metal Bond Formation

Part of our program in the synthesis and characterization of new solid state materials with interactions between directly-bonded metals involved the development of a versatile and convenient reagent for the synthesis of polymetallic complexes with metal-to-iron covalent bonds. The new reagent, bis(chloromercury)tetracarbonyliron and zinc metal in diglyme. Unlike the insoluble, air-sensitive alkali metal salt, $Na_2Fe(CO)_4$, commonly used as a synthetic intermediate, $(ZnCl)_2Fe(CO)_4$ is soluble in ethereal solvents and exhibits substantial stability in air. Thus far it has been used to prepare several metal-metal bonded derivatives of the type $(RR'_2Sn)_2Fe(CO)_4$ where R' is n-butyl and R is n-butyl, phenyl or benzyl.

Research supported by the Materials Science Center.

HIGHLIGHTS

A single crystal x-ray diffraction study of the complex, $Zn_2Co_4(CO)_{15}$ revealed the first case of zinc incorporated in a transition metal cluster. Another zinc complex $(ClZn)_2Fe(CO)_4$(diglyme) was prepared and shown to be a useful synthetic intermediate for metal-to-metal bond formation. Phosphinate complexes of divalent chromium and molybdenum showed a wide variety of magnetic moments ranging from the high spin complex $[Cr(O_2PPh_2)_2]_n$ (4.6 B.M.) to the diamagnetic $[Mo(S_2PPH_2)_2]_n$. The last named compound is the first example of a dithiophosphinate complex of a divalent Group VI metal.

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Structure and Properties of Sodium Beta Alumina

The properties of sodium beta alumina solid electrolyte have been studied as affected by impurities. The effects of Ca, Si and Zr on the ionic conductivity have been quantitatively determined. Zr and Si form partially blocking intergranular phases. Si is also partially taken up in the crystal lattice. The effect of Ca is more complex, and varies significantly with the heat treatment of the sintering operation. Ca is more deleterious than Si, and was shown to concentrate at grain boundaries, leading to intergranular rather than transgranular fracture. The microstructure of the β alumina was examined in detail by means of transmission and scanning electron microscopy. Possible ionic current concentrations at low angle tilt boundaries have been discussed.

Research supported by the Electric Power Research Institute and the Materials Science Center.

Reduction of Mixed Spinel Oxides

Cobalt and nickel ferrites have been alloyed with aluminum or magnesium ions, and their reaction rates with hydrogen have been studied. Thermogravimetrical analysis showed that the reaction kinetics are complex. Initially there is a rapid transient, after which the kinetics follow a t^n dependence where $1/2 < n < 1$. Optical studies show that the porosity in the reaction layer is significantly affected by the alloying elements.

Research supported by the Energy Research and Development Administration.

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Na_xWO_3

The work on this material has been carried out by B. R. Weinberger through a study of the NMR properties of the W^{183} spin system over the range of x-values from x=0.22 to x=0.85. He has obtained a full set of values of relaxation times at 4.2K and 1.3K, and a set of line shapes at 1.3K. The most significant new information comes through the resonance line shapes. These show very clearly that the tungsten nuclei in the material experience a broad and essentially random distribution of local values of the Knight shift, and give strong evidence that the picture of condensation of Na atoms into a Na-rich condensate, recently put forward by Webman, Jortner and Cohen, is almost surely wrong.

Alkali-Gold Intermetallic Compounds

In the past year, we have been able to prepare and study powders of the two materials, CsAu and RbAu. Measurements to date have included x-ray studies of crystal structure of the powders and NMR experiments studying the Cs^{133} spin system in CsAu and the Rb^{87} spin system in RbAu. The most interesting NMR results to date support previous interpretations that CsAu is a semiconductor, and provide that RbAu is a metallic system. The NMR for RbAu shows a Knight shift of about 0.18% at room temperature, a value which changes only slightly as the sample is cooled to helium temperature. This number is appropriate to a metallic state for RbAu. The x-ray patterns for the RbAu powders show a clean CsCl structure, and we believe that the stoichiometric RbAu is, indeed, metallic — or perhaps more properly, semi-metallic. If, indeed, the metallic transition in the series LCsAu, RbAu, KAu occurs between the first two members of the series, we expect to have some success in pursuing our study of this phenomenon, since both of these materials should be substantially easier to handle than KAu. Just at the end of the 1975-1976 year, we began work to prepare thin films of crystalline RbAu, and we expect to move to transport property measurements as well as more extensive NMR measurements during the 1976-1977 year.

Research supported by the National Science Foundation and the Materials Science Center.

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Nonlinearity in Physical Systems

Structural Phase Transitions

Nondestructive Evaluation

Theoretical studies of structural phase transitions leads to new insights on how "solitary structures" or "solitons" may manifest themselves in both the structure and dynamics of condensed matter. This topic, begun in 1973-1974, continues to be a most active subject in many disciplines. Manifestations are being found simultaneously in many other fields: in structural phase transitions, metallurgy, nonlinear quantum field theory, plasma physics, quantum electronics, and chemical reactions — indeed the ubiquitous nature of the viewpoint has led Haken to organize these as a subject called "Synergetics". It is planned to continue studies in this area for some time.

In another quite distinct applied area we have taken ideas built upon several years of basic theoretical research which would not have qualified as a thrust topic at the time, and which indeed ARPA chose not to support, and under support from Rockwell International have made several direct applications in support of their non-destructive materials evaluation program.

We developed and programmed an integral equation formulation of the ultrasonic scattering problem. We have compared the results of the Born approximation with exact results for spherical scatterers. From that study we learned much about the regions of applicability and validity of the Born Approximation.

Recently we have completed the formal theoretical work, and have placed special emphasis in attempts to make contact with the experimental situation for laboratory prepared flaws in determined geometries — (a step closer to the "real world"). In particular we identify some general features or indices that might be useful in evaluation of scattering data for NDT.

This program continues.

Research supported by the Energy Research Development Administration, Rockwell International, the National Aeronautical and Space Administration and the Materials Science Center.

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Thermal Properties of Highly Disordered Solids

It has been claimed in the literature that mixed crystal KBr-KI (50:50) crystallizes in a bromine-rich, and iodine-rich, and in a 50:50 mixed phase. The crystallites are of ~1000Å diameter. Because of the large differences in the speeds of sound in the three phases, this material should exhibit a very low thermal conductivity, comparable to that of glasses. The experimental result, however, is that conductivity is similar to that expected for a uniformly mixed crystal or of a crystal consisting of large crystallites, of more than 10,000Å diameters. X-ray fluorescence experiments so far have failed to show such large crystallites. This work is continuing.

We have also searched for a low temperature specific heat anomaly in plastically deformed lead, in an attempt to study the influence of dislocations. So far, the result has been negative. The specific heat of cold-worked lead agrees with that obtained in high purity single crystals.

Research supported by the Materials Science Center.

Search for Amorphous Oxygen

We have assembled a sensitive magnetic susceptibility bridge and have found hysteresis effects near the solidification temperature, as well as near the temperatures of magnetic phase transitions. Some of the evidence points towards the existance of an amorphous phase, but the evidence is inconclusive. Work in an applied d.c. magnetic field is presently underway.

Research supported by the Advanced Research Projects Agency.

Amorphous Solids

High energy neutron irradiation raises the thermal conductivity of vitreous silica. This effect, whose origin is unknown, and which represents the first instance in which we have been able to influence the thermal conductivity of an amorphous solid, has been found to be closely related to the neutron-induced densification of the silica. The specific heat of irradiated silica is practically unchanged. This indicates that the relation between anamalous specific heat and the scattering of the phonons is not as close as previously assumed.

We have measured the thermal conductivity of $MnO \cdot Al_2O_3 \cdot SiO_2$, magnetic glass, with a very large specific heat anomaly at low temperatures. The conductivity is indistinguishable from that of any non-magnetic silica based glass; the magnetic excitations appear to have a negligible influence on heat transport.

Research supported by the Energy Research and Development Administration.

HIGHLIGHTS

The insensitivity of the conductivity of amorphous solids to the chemical composition or to the presence of other excitations continues to remain the most surprising puzzle.

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The Properties of New Materials Including One Dimensional Systems

The past year, my first at Cornell, has been concerned mainly with the setting up of a new laboratory. The building of the first pieces of apparatus is nearing completion as we enter the phase of testing the performance of the equipment. Two main experiments have been set up to measure magnetic susceptibility as a function of temperature and to investigate paramagnetic relaxation rates.

The principal development of new materials will be in the area of organometallic polymers, specifically poly (metal phosphinates), in a collaboration begun with J. M. Burlitch. The focus is the understanding of the solid-state interactions in such materials with a view to developing polymers with desirable electric and magnetic properties. As linear polymeric systems, these materials bear many properties peculiar to one dimension, hence our continuing interest in this area of solid state physics.

One experiment, done in collaboration with H. Temkin, has been completed. We attempted to observe light scattering from solitons in TTF-TCNQ at low temperature. Our results, though negative, put limits on some properties of these excitations, which have been the subject of extensive theoretical research in non-linear field theories.

Research supported by the Materials Science Center.

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Superconductivity in Nonstoichiometric Compunds, Layers and Chalcogen Ternaries

Phase Relations and Compound Formation in Metal-Ammonia Systems

Cooperative Electron Phenomena in Two-Dimensional Materials

This is an experimental program to study the chemical manipulation of electron transport and magnetic interaction at the metal-nonmetal transition. One part of the program is devoted to the synthesis, structure characterization, and electrical property measurement of layer, tunnel-structure, and cluster compounds; the other, to magnetic and magnetic resonance study of "expanded metal" systems. Ultrahigh-purity materials are produced by vapor phase transport, flash rf induction, and electrochemical deposition. Electrical conductivity, Hall voltage, thermal emf, magnetic susceptibility, and ESR are investigated over the range 1.5-300°K. Special attention is given to the effect of nonstoichiometry, cation-for-cation and anion-for-anion substitution, and additive intercalation on the superconducting transition.

Research supported ty the Air Force Office of Scientific Research, the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

(1) The electrical conductivity, static magnetic susceptibility, and Hall voltage have been measured from room temperature to liquid helium on a series of carefully characterized vanadium-substituted niobium diselenides ($Nb_{1-x}V_xSe_2$, $0<x<0.30$). Relatively large temperature-dependent Pauli paramagnetism and quadratic dependence of resistivity at low temperatures suggest a strongly correlated electron gas. Anomalies in the Hall voltage and resistivity are consistent with a charge-density-wave transition. The effect of vanadium substitution is mainly to change the nature of the coordination from trigonal prismatic to octahedral and, thereby, the component layers of the polytype structure. The superconducting critical temperature was observed to drop strongly in the 2H phase and then flatten out as progressive vanadium substitution is accommodated in layers with octahedral coordination.

(2) Powder samples of ultrapure stoichiometric VSe_2 have been made by direct synthesis. Single crystal specimens have been made by vapor phase transport in the presence of iodine. X-ray characterization indicated only the 1T polytype. Behavior was metallic over the range 1.5 to 300°K, but there were discontinuities at about 100°K in resistivity, magnetic susceptibility, and Hall voltage. These are apparently due to the onset of charge density waves. Below 50°K, there was a clear quadratic dependence on temperature which combined with relatively high Pauli paramagnetism to indicate Baber-type-electron-electron scattering. No superconductivity was observed down to 1.5°K.

(3) ESR studies on the semiconductor V_3O_7 over a range of temperature reveal the existence

of paramagnetic V^{4+} ions with resolved hyperfine splitting in the interval 10-12°K. The observed hyperfine structure can be interpreted in terms of an induced Fermi contact interaction whereby a single d-electron produces an inbalance in the paired, inner-shell, s-electron states. Computer simulations indicated that the unpaired electron wavefunction encompasses some 13-14 lattice sites.

(4) A series of dysprosium hexaborides in which dysprosium was progressively replaced by ytterbium have been prepared. Magnetic susceptibilities in the interval 63-300°K follow Curie-Weiss laws with progressively decreasing Weiss constant as ytterbium contact increases. Below 60°K, the materials are antiferromagnetic. Interpretation of the results via statistical analysis of two, three, and greater-than-three clusters indicates that when isolated magnetic ions are corrected for, the residual magnetism corresponds to a constant exchange energy J, independent of conduction electron concentration. There is no direct evidence that indirect exchange plays a role in the magnetic interaction.

(5) A new layered compound HfTeI has been synthesized. The iodine atom apparently substitutes at random for tellurium in the chalcogen layer, and its extra electron goes into the empty conduction band to give a VB-like metal. Detailed electrical and structural studies are in progress.

(6) The conditions of niobium disulfide synthesis have been investigated over a wide range of starting stoichiometry and temperature conditions. All the preparations have yielded non-stoichiometric products, even up to 7.5 atm excess sulfur pressure. It is believed that all literature results on NbS_2 need to be questioned and that excess niobium is thermodynamically needed to counter electrostatic instabilities. Highly unusual mechanical properties have been noted. A new polytype of rhombehedral symmetry has been discovered.

(7) The full series of selenium-substituted molybdenum disulfides has been prepared. Although the end members are nonmetals as expected, the middle numbers appear to be metallic. X-ray studies have been completed; they indicate full range solid solubility with an unusual maximum in the interlayer: intralayer spacing ratio. The effect on magnetic doping and intercalation-induced superconductivity is being examined.

(8) Tunnel-structure ammonium tungsten bronzes have been prepared over a wide range of conditions (temperature, time, crystallinity, composition of a vapor phase). None of the previously reported structure and superconductivity findings can be reproduced. It is believed that the material as reported in the literature does not exist and the reported properties pertain to an undefined mixture of lower oxides of tungsten.

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Infrared Properties of Metals, Semimetals and Semiconductors

Electromagnetic surface waves have been launched on metal surfaces using CO_2 laser radiation together with a prism coupler. We are now developing the capability to use an infrared interferometer in this configuration for spectroscopic measurements of surface states.

The far infrared spectra of small (100Å) metallic particles are observed to have the same frequency dependence independent of metallic element or particle size. The absorption does increase with increasing filling factor and this dependence is now under investigation.

We have continued our study of the far infrared properties of thick slabs of bismuth by means of the Faraday transmission technique. High resolution studies of the different electronic excitation of the holes has been made both with Fourier transform interferometry and also far infrared laser radiation.

We have also studied cyclotron resonance in InSb and an InSb:NiSb eutectic using $10\mu CO_2$ laser radiation and a 500 k gauss pulse magnet.

Research supported by the Energy Research Development Administration and the Materials Science Center.

Experimental Phonon Physics

We have continued our study of the temperature dependence of the far infrared spectra of a variety of glasses in order to identify the specific energy level schemes of the anomalous low frequency modes. This year's studies on AsS_3, $AsSe_3$ and Se provide experimental data which is similar to that previously obtained for SiO_2, GeO_2 and PMMA.

Research supported by the Energy Research Development Administration.

Solar Energy

In order to develop a solar energy transformer, the optical properties of composite structures are being investigated.

Research supported by RANN and the Materials Science Center.

Absorption in Highly Transparent Media

The absorption processes in ultrapure KBr are being identified by combining calorimetric and infrared Fourier transform techniques.

Research supported by AFCRL.

Infrared Techniques

A multiuser fast Fourier transform computer system is being developed for simultaneous use with the near and far infrared spectrometers.

Research supported by Energy Research Development Administration, RANN, AFCRL and the Materials Science Center.

HIGHLIGHTS

I. E and M surface waves in the 10 micron wavelength region propagate a few cm on metal surfaces. In the far infrared spectral region the waves propagate for distances on the order of meters.

II. Cyclotron resonances have been observed at 10 microns in a InSb:NiSb eutectic. The NiSb rod-like structure lowers the crystal symmetry but many of the transitions previously observed in pure InSb also appear in this two phase structure.

III. Surface absorption states have been observed at 9.5 micron wavelength in ultrapure KBr single crystals. Total internal reflection spectroscopy is being used to study these centers.

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"Some One and Two Dimensional Experiments in Three Dimensional Solids," A. J. Sievers, MSC Report 2643 (1976). Submitted for publication.

"Polarization Flipper for Infrared Laser Beams," A. R. Chraplyvy, MSC Report 2646 (1976).

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"Far Infrared Properties of Lattice Resonant Modes VI. Hydrostatic Pressure Effects,: A. M. Kahan, M. Patterson and A. J. Sievers, MSC Report 2674 (1976).

Exploratory and Continuing Programs

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Investigations into Theories of Metals and Alloys

My materials oriented research during the past year has been centered on (a) calculations of equations of state and elastic properties of simple metals, (b) a study of the phonon structure factor and its application to x-ray scattering from metals, (c) a study of compound formation in certain liquid alloys of simple metals, and (d) the theory of the transport properties of small particle composites.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

1. We have completed calculations of pressure versus lattice constant for the simple metal Al: this equation of state may vie with the sodium chloride scale, particularly in the megabar region.

2. We are able, with a non-expansion technique to calculate the density-density correlation function for a simple metal disturbed by phonons. An application to x-ray scattering shows that the measured cross-section may contain significant information on effective electron-ion interactions.

3. The stability of liquid alloys against phase-separation, fusion, and compound formation can be expressed in terms of the behavior of the partial structure factors $S_{\mu\beta}(\underline{k})$ as functions of the relevant thermodynamic variables. We have made progress in calculating the $S_{\mu\beta}(\underline{k})$ in terms of the fundamental (self-consistently screened) electron-ion interactions.

4. In the area of composites, we have investigated the optical response of metal-insulator mixtures using effective medium theory. For correlated 3-component systems in which the metal particles are coated with oxides, substantial effects in the optical conductivity are predicted. We have also been examining certain formal questions connected with the effective medium approach.

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Magnetic Phenomena and the Transport Properties of Metals

Part of this program involves the study of the propagation and generation characteristics of plasma and acoustic waves in solids and the use of these phenomena as a probe to study the electronic properties of metals. The remainder of the program uses a variety of mutual impedance, radio-frequency size effect, and electrical and thermal conductivity measurements to elucidate various scattering mechanisms in metals. Helicon and acoustic wave measurements are made using pulse and c.w. techniques. Most measurements can be carried out in any desired temperature range from 1.5 to 300K in magnetic fields up to 100 kG.

Research supported by the National Science Foundation, the Energy Research Development Administration, Rockwell International and the Materials Science Center.

HIGHLIGHTS

A study of various radio-frequency size effect (RFSE) measurement techniques has been completed to determine the effect of the mode of excitation on the electron-phonon scattering rate determined from the measurements. In particular, the marginal oscillator technique, involving bilateral excitation of the specimen, was compared to the transmission technique, involving unilateral excitation. No observable difference was found in the scattering rates measured by the two methods, indicating that either technique can be used when most suitable.

An extended temperature range (2K - 13K) cryostat has been constructed to allow RFSE measurements of the electron-phonon scattering rate in aluminum. Techniques for cutting and polishing the specimens have been developed, and measurements are now underway. The aim of this research is to determine the magnitude and anisotropy of the electron-phonon scattering rate over the Fermi surface, and to understand both in fundamental terms.

The use of electromagnetic acoustic-wave transducers (EMATs) as a noncontact method of producing ultrasound has suffered from insufficient detailed knowledge of the acoustic field resulting from coils of varying geometries. In particular, it is known that the insertion loss varies according to the coil geometry employed. In order to more fully exploit the many unique characteristics of EMATs, we are studying the displacement field or acoustic mode patterns generated by various coil geometries. These patterns are sensitive to many of the parameters that must be optimized in order to obtain an efficient and useful electromechanical transducer. The simplest practical geometry for which exact calculations are possible is a planar spiral coil. We have utilized an EMAT as a detector in an experimental scanning system to measure the mode patterns of coils. For the planar spiral coil, there is good agreement with exact calculations.

To date, all work on bulkwave EMATs has utilized large permanent magnets or electromagnets. This places rather severe restrictions on the uses of EMATs. The development of high

energy product rare earth-cobalt permanent magnets has made possible the design of compact (250 gram) yet sensitive EMATs. We have designed and tested a number of units and compared their performance with a simple yet practical model which we developed. All the main performance characteristics can be explained.

REPORTS AND PUBLICATIONS

"Observations on the Determination of Electron Mean Free Paths from RF Size Effect Measurements", D. K. Wagner and R. Cochran, Phys. Cond. Matter 19, 351 (1975).

"The Electron-Phonon Mean Free Path in Potassium: A Comparative Study of Radio-Frequency Size Effect Measurement Techniques", M. D. Rosenthal and D. K. Wagner, J. Phys. F: Metals Physics 6, 413 (1976).

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"The Electron-Phonon Mean Free Path in Potassium: A Comparative Study of Radio Frequency Size Effect Measurement Techniques", M. D. Rosenthal and D. K. Wagner, MSC 2632 (1976). See; Metal Phys. No. 36 (1976).

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Photochemical Studies of Photosynthetic Reaction Centers

The photochemistry of photosynthesis occurs in reaction centers (RC's) that can be isolated from photosynthetic bacteria as specific pigment-protein complexes. Each RC particle contains four molecules of bacteriochlorophyll (Bchl), two of bacteriopheophytin (Bph), and two ubiquinone (UQ). In the past three years we have discovered that when the Bchl is driven into its lowest excited singlet state, this state is converted within 10 psec into a biradical state (termed p^F) in which an electron has been displaced from Bchl to Bph. This process involves two of the four Bchl and one of the two Bphs, generating a radical-pair of the type $(Bchl)_2^+ \cdots (Bph)^-$. The electron moves on from Bph to one of the UQ molecules with half time about 200 psec, giving $(Bchl)_2^+\cdot$ and $UQ^-\cdot$ as photochemical products that are stable for 20-100 msec against back-reaction. In the living cell the electron moves on through "secondary" UQ and cytochromes, eventually returning to $(Bchl)_2^+\cdot$ and restoring it to its neutral state. The energy released in this cycle of electron flow is used for all the energy-requiring processes of the cell. Collection of light energy is aided by an "antenna" of Bchl, about 20 molecules for each RC, that absorbs light and transfers the quanta of singlet excitation energy to the RC. The Bchl of the antenna is bound to a protein distinct from that of the RC.

We are exploring details of the structure and photochemical mechanism in these RC's.

We have shown that the quantum efficiency of Bchl oxidation in RC's is ≥ 0.9 at temperatures down to 4K. The quantum yield of Bchl fluorescence in RC's, about 10^{-3}, is also independent of temperature (±10 per cent) down to 40K. This shows that either the fluorescence comes exclusively from the primary excited singlet state of Bchl, and not at all through a back reaction from the p^F state to excited singlet, or else the energies of excited singlet and p^F are equal within 10^{-3} ev.

We have studied the reconstitution of excitation energy transfer from antenna pigment-protein to RC's when these purified components are mixed. Transfer efficiencies close to 100 per cent are easily achieved, judging from the quantum efficiency of RC photochemistry driven by light absorbed by antenna Bchl. Yields of fluorescence from antenna Bchl in these mixtures are comparable to those in the native tissue: about 1 per cent when the RC's are photochemically active and 3 per cent when the RC's have been rendered inactive and are therefore less effective in quenching excitation energy from the antenna Bchl. These values are consistent with estimates of the lifetime of the excited singlet state of Bchl in isolated RC's, 7 psec in the active state and 20 psec at redox potentials low enough to reduce the UQ that acts as electron acceptor. The measurements with antenna + RC indicate that the rate of quenching of excited singlet energy by photochemically inactive RC's is the same whether the RC's have been inactivated by reducing the UQ-electron acceptor or by oxidizing the Bchl that serves as electron donor.

We have measured optical linear dichrosim (polarized absorption) in oriented samples of

photosynthetic membrane fragments, prepared by drying these fragments onto glass slides. These measurements give information about the orientations of optical transition moments for the chromophores of the antenna pigment and of the RC. The results indicate that the tetrapyrrole planes of both the electron-donor Bchl and the Bph in the RC are approximately perpendicular to the plane of the membrane. These measurements have also helped us to detect the dimeric absorption band structure of the "special pair" of Bchl molecules that share the electron donating function, and the nonomer band of this pair in the singly oxidized state $(Bchl)_2^{+}\cdot$.

Measurements of light-induced changes in the optical absorption spectrum of RC's reveal the reduction of the UQ that serves as primary electron acceptor. We have studied subsequent electron transfer, from "primary" to "secondary" UQ, by the same means. RC's were mixed with an excess of secondary electron donor such as tetramethyl phenylene diamine, which serves to reduce the $(Bchl)_2^{+}\cdot$ rapidly after it has been formed photochemically. The other photochemical product, $UQ^{-}\cdot$, could be allowed to interact with added UQ. We exposed this system to a sequence of brief laser flashes separated by several seconds. $UQ^{-}\cdot$ was formed after flashes 1, 3, 5, $\cdots$, and was stable in the dark for many seconds. This $UQ^{-}\cdot$ was made to disappear by flashed 2, 4, 6,$\cdots$ A new molecule of the fully reduced UQH_2 was formed after every even-number flash. If no UQ was added, so that the RC's contained only the two native molecules of UQ, an oscillation (formation and disappearance of $UQ^{-}\cdot$) was observed on only the first two flashes. After that a flash generated $UQ^{-}\cdot$ that relaxed to UQ rapidly in the dark. We interpret these results through the following reaction sequence, which indicates how the "one-electron" photochemistry is translated into a "two-electron" reduction of secondary UQ. The Bchl special pair is represented by B, and two UQ's by Q_1 and Q_2.

$$B.....Q_1.....Q_2$$
(first flash)

electron from donor $\rightarrow B^{+}....Q_1^{-}....Q_2$
(dark)

$$B.....Q_1.....Q_2^{-}$$
(second flash)

electron from donor $\rightarrow B^{+}....Q_1^{-}....Q_2^{-}$
(dark)

$$B.....Q_1.... Q_2^{=}$$

This is followed by a reaction with added, or "secondary pool" UQ:

$$Q_2^{=} + 2H^{+}\ UQ \rightarrow Q_2 + UQH_2$$

restoring the RC to its starting configuration. These have been the first definitive experiments about the "quinone cycle" in photosynthetic bacteria.

In collaboration with Professor Aaron Lewis and his associates we have measured the quantum efficiency of fluorescence from bacteriorhodopsin at temperatures down to 40K. At temperatures below 150K the fluorescence increases strongly with decreasing temperature. These new data can be correlated with data on the fluorescence lifetime so as to predict the intrinsic lifetime of the excited state, and thus to give information about the nature of this excited state.

Research supported by the Energy Research and Development Administration, the National Science Foundation and the Materials Science Center.

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"Photochemical Quantum Efficiency and Absorption Spectra of Reaction Centers from Rhodopseudomonas Sphaeroides at Low Temperature," R. K. Clayton and T Yamamoto, Photochem. Photobiol 24, 67-70 (1976).

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"Secondary Electron Transfer in Reaction Centers of Rhodopseudomonas Sphaeroides." A. Vermeglio, Biochem. Biophys. Acta., in press (1976).

"Photosynthesis and Solar Energy Conversion," R. K. Clayton, Brookhaven Symposia in Biol. No. 28, in press (1976).

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Spin Resonance and Dynamical Structure Studies

This program is a combined experimental and theoretical study of spin resonance providing insight into a wide variety of relaxation phenomena. Specific projects include: 1) Studies of Dynamical Structure of Liquids and Frozen Media and Molecular Diffusion Processes by ESR; 2) Studies of Dynamical Structure of Liquid Crystals and Molecular Dynamics at Order-Disorder Phase Transitions; 3) Pressure-Dependent Studies of Dynamical Structures of Liquids and Liquid-Crystals; 4) Studies of Radical Dynamics on Surfaces and Surface Catalysis by ESR; 5) Studies of Polymer Structure and Dynamics by ESR; 6) Studies of Reactive Molecular Energy Transfer in Liquids by Chemically-Induced Dynamic Electron-Spin Polarization.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

We have, in our recent pressure-dependent studies on PD-Tempone in a nematic liquid crystal solvent, shown that such studies are very useful for obtaining thermodynamic data associated with the ordering of the spin probe, which may be utilized to test equations of state for the liquid crystalline phase as well as the nature of the orienting potential. Thus, for example, we were able to show that the orienting potential of PD-Tempone in a nematic solvent is essentially independent of molar volume V, although recent PVT work indicates a $V^{-3.5}$ dependence for the liquid crystalline molecules. Our result is consistent with our model of the probe in a "cavity" in the liquid-crystalline structure.

We were also able to show in our pressure-dependent work, that the motional narrowing relaxation results as well as the "pressure-induced" slow-tumbling results yield the virtually identical anomalies seen in previous studies as a function only of temperature. The close relationship between our observed anomalies and the τ_R-values, independent of whether these τ_R-values are achieved by reduced temperature or increased pressure, appear to confirm our theory that they are due to fluctuating intermolecular interactions which relax on a slow time-scale: i.e., the slowly-relaxing local-structure mechanism. This mechanism of a probe or solute molecule reorienting relative to a persistent potential, which then relaxes on a slower time scale, is expected to be a very general one in liquid crystals and plastic crystals, structured liquids, and biological systems.

In our recent experiments at the isotropic-nematic phase transition utilizing careful temperature control, we have found that the ESR linewidth parameters behave anomalously as the phase transition at temperature T_c is approached from either side. In fact the width parameters appear to diverge. We have successfully analyzed the anomalous contributions in terms of Landau-de Gennes mean-field theory for the weak first order transition, as applied to ESR relaxation. That is, both the magnitude of the effect, and the critical exponent, are in close agreement with

the theory. Most importantly, these observations display a symmetry about T_c fpr spin-relaxation due to critical fluctuations, which is expected from simple theory, but has not previously been demonstrated experimentally.

We have recently adapted our three dimensional theory of CIDEP and CIDNP to two dimensions. These results are expected to be of importance in magnetic resonance studies of reaction dynamics on surfaces and interfaces. Our predictions are that in two dimensions, because radical-pair time-integrated re-encounter probabilities are unity, the dynamic nature of the spin-polarizing mechanism is vastly different from that for three dimensions. We have developed approximate analytic expressions for such effects, which show that the spin polarizations approach their maximum possible values asymptotically essentially with lnt (t=time), unless interfered with by other processes.

REPORTS AND PUBLICATIONS

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"The Theory of Chemically-Induced Dynamic Spin Polarization," J. H. Freed and J. B. Pedersen, Adv. Mag. Res. 8, 1-84 (1976).

"Dynamic Effects of Pair Correlation Functions on Spin Relaxation by Translational Diffusion in Liquids," L. P. Hwang and J. H. Freed, MSC Report 2560 (1975). See; J. Chem. Phys. 63, 4017-4025 (1975).

"An ESR Study of the Pressure Dependence of Ordering and Spin Relaxation in a Liquid Crystalline Solvent," J. S. Hwang, K. V. S. Rao and J. H. Freed, J. Phys. Chem. 80, 1790-1801 (1976).

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"An Electron Spin Resonance Study of Rotational Reorientation and Spin Relaxation in Liquid Crystal Media," C. F. Polnaszek, Ph.D. Thesis, MSC Report 2601 (1976).

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Statistical Physics of Disordered Systems

This program is directed towards a theoretical understanding of fluctuations in systems where randomness and coherence are subtly mixed. The emphasis is on systems far from thermal equilibrium. During the past year work has continued on the anomalous thermal properties of glasses at low temperatures, on the theory of fully developed hydrodynamic turbulence, and work has begun on the theory of superfluid turbulence. In all cases the emphasis has been on phenomenological theory with explicit suggestions for experimental tests of the theoretical ideas.

Research supported by the National Science Foundation and the Materials Science Center.

HIGHLIGHTS

I. The anomalous thermal properties of glasses have been reviewed, and a quasi-macroscopic origin for the tunneling modes has been suggested. Originally this was phrased in terms of a possible array of dislocations in the glassy state, and the ultra-small angle scattering of x-rays was suggested as an experimental test. Experiment does not support the idea in its naive form, but a structural origin of the tunneling modes remains plausible.

II. A dynamical non-linear cascade model for fully developed turbulence has been developed which could plausibly play the role of a mean field theory for a true dynamical theory. The model contains a free parameter which could in principle be calculated from the Navier-Stokes equations. The scaling form of the solutions is explicitly demonstrated, and an interesting cross-over phenomenon between forward and backward cascades in k-space is observed.

III. A theoretical investigation has begun attempting to extend the Vinen theory of superfluid turbulence in helium counterflow. Recent experiments by Tough and collaborators at Ohio State show an unexplained extra pressure drop in the turbulent regime, and a second threshold associated with the onset of normal fluid fluctuations. A crude prediction of the channel diameter dependence of the second threshold has been given, but there is as yet no experimental information. This is the beginning of an extended investigation of superfluid turbulence as a basic tool for the understanding of turbulent fluid flow. This must be considered as exploratory for the present.

REPORTS AND PUBLICATIONS

"Models for Thermal and Vibration Properties of Glasses at Low Temperatures," M-S Lu, Ph.D. Thesis, MSC Report 2501 (1975).

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High Energy Electron Spectroscopy and Velocity Analyzing Electron Microscopy of Aluminum

Mr. Batson's Ph.D. thesis work was completed during this year. A partial report was given last year detailing our efforts to measure $\varepsilon(q,\omega)$ into the region where plasmon excitations change to single particle excitations. We were successful in this task producing $\varepsilon(q,\omega)$ over a range $0<h\omega<100eV$ with a resolution ~1eV and over a range $0<q<3.1\mathring{A}^{-1}$ with a $\Delta q \sim 0.1\mathring{A}^{-1}$. New experimental techniques developed during the year include the use of high brightness LaB_6 electron filaments. In addition, to make precise cross-section measurements, we found it necessary to use computer controlled scans to focus the condenser lens system of the electron microscope. During the year, our computer programs designed to rid the spectrum of multiple scattering were refined to the point at which considerable confidence emerged. Essentially two main procedures were used. One used an image-loss profile to provide an integrated energy-loss spectrum for use in deconvoluting wide-angle quasi-elastic scattering. Once this was accomplished, conditions were favorable for the use of Fourier transform techniques in deconvoluting the single scattering function from the multiple scattering. The results show nicely the onset of Landau damping as the plasmon enters the single particle region and shows the eventual emergence of single particle excitations as the dominant aspect. Our results are qualitatively consistent with RPA concepts although detailed comparisons call for more extensive theoretical computations than are at our command. It appears evident, however, that previous experimental work has overlooked small but significant multiple scattering corrections.

Anisotropic Materials

Exploration of anisotropic effects and materials has proceeded apace. Magnesium proved to be isotropic, graphite and polymeric $(SN)_x$ proved to be highly anisotropic.

Interband Transitions

During the year studies were begun of the q-dependence of an interband transition in Al. These studies are still under way.

Research supported by the Materials Science Center.

REPORTS AND PUBLICATIONS

"Plasmon Dispersion and Anisotropy in Polymeric Sulfur Nitride, $(SN)_x$," C. H. Chen, J. Silcox, A. F. Garito, A. J. Heeger and A. G. MacDiarmid, Phys. Rev. Letters 36, 525 (1976).

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"Electron Energy Losses in Silicon: Bulk and Surface Plasmons and Cerenkov Radiation," C. H. Chen, J. Silcox and R. Vincent, Phys. Rev. B12, 64 (1975).

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ESR Studies of Metals

Our principal effort in metals now focusses on studying the transmission electron spin resonance (TESR) of metal bilayer samples. Our aims are to assure that the phenomenology of these experiments is understood, to obtain information about spin relaxation in metals in which ESR cannot be directly observed, and to obtain information about the transport of spin magnetization across the interfacial boundary.

One experiment in progress involves the study of the weak ferromagnet, Pd:Fe, evaporated onto a copper foil. Control of the Curie temperature via the Fe concentration allows measurements both above and below T_c, and will help confirm or deny existing models for the theory of these experiments. A second experiment involving a Nb film on copper is interpreted tentatively as demonstrating that the development in the Nb of the superconducting energy gap at low temperature prevents the diffusion of magnetization across the interface.

We have also spent considerable effort in the search for ESR in small (50Å) aluminum particles prepared by the group of Professor Buhrman. In view of our quite adequate sensitivity and the carefully characterized aluminum particles our negative results must be considered as throwing considerable doubt on the interpretation of the experiments of other groups purporting to have seen ESR in small particles.

Research supported by the National Science Foundation and the Materials Science Center.

ESR in Insulators

We have completed a preliminary study of the Cr^{++} pair spectrum in a chromium phosphinate dimer closely related to the magnetic polymers under investigation by Professor Scott and Burlitch. The interpretation of these results have yielded both the intrapair exchange energy and values for the crystal field splitting.

REPORTS AND PUBLICATIONS

"Transmission Electron Spin Resonance Measurements of Spin-Flip Scattering and Crystal Field Parameters in Dilute Al: Rare Earth Alloys," S. A. Dodds, Ph.D. Thesis, MSC Report 2436 (1975).

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II. CENTRAL FACILITIES
1975-76

The creation and operation of a vigorous and modern central research facility system is an essential MSC function. A significant fraction of the Center's resources have over the years been allocated to these communal laboratories. The central facility system allows individual research groups access on an organized basis to a full spectrum of modern research equipment. Among the further advantages of the system are, 1) Major capital equipment, increasingly expensive and difficult to obtain, can be scientifically justified and more easily financed on a general use basis. 2) A high quality technical staff can be recruited, for the maintenance of complex equipment, and the development and transmission of accummulated experimental wisdom, and 3) Graduate student education is facilitated by exposure to a wide range of modern research equipment and techniques.

The cost of operating the central facility system is partially offset by "income" each facility obtains by charging for its labor and services. No attempt is made to recover all costs. However, in addition to acquiring some income, the charging system does provide one index of the relative usefulness of each facility to the Center membership. Charges are levied for routine services, major equipment use, and materials consumed, but are only nominal for development work which extends the facilities' capabilities. Income for 1975-76 was $198,000, with 32 per cent from Center budgets and 68 per cent from other grants and contracts.

Continued development and utilization of the MSC Computing Facility was a major activity in 1975-76. Its primary purpose is to facilitate experimental programs by providing efficient computing facilities for on-line and off-line data acquisition and analysis. The heart of the system is a Prime 300 multi-user computer, with a 60 million byte disc and tape drive, which was acquired in the fall of 1975 and became operational in December. Experience with the system has been most satisfactory, with very little downtime and a use level well beyond expectations.

The reports of the individual facilities follow.

REPORT FOR THE MSC ANALYTICAL FACILITY for the period 7/1/75 to 6/30/76.

1. Clients Served.

The Analytical Facility has continued its progress this year. Total business has increased by 150% over last year and four times over 1973-1974. More than 400 samples were analyzed this year for 31 investigators; of these 14 were MSC and 12 were non-MSC scientists. Also, samples for five non-Cornell groups were analyzed. Practically all the elements in the periodic table other than transuranic, artificial or inert gas elements were determined by the techniques of wet chemical analysis, atomic absorption and flame emission spectrometry, optical emission spectrography, spectrophotometry, spark source mass spectrometry and neutron activation analysis, both instrumental and radiochemical. The types of samples analyzed include high purity metals, alloys, inorganic compounds, geological and biological materials, and environmental samples such as water and sediments. A list of the actual analyses carried out is given below.

Investigator	Dept.	Analysis (No. of Samples)	Methods Used
B. F. Addis	M.S.E.	Ni, Mo in wires (4)	WC
		Impurities in Fe and Cu (2)	ES
Agway, Ithaca	-	Anal. of Fertilizers (3)	AA
D. G. Ast	M.S.E.	Bi in Pb.Bi alloy (1)	AA + WC
J. Bass	Univ. Michigan Lansing, Mich.	Impurities in W rods (5)	SSMS
B. Bonnichsen	Geology	Anal. of Duluth Complex rocks (24)	AA + RNAA
J. M. Burlitch	Chem.	Cl,Br,Al,Sn,Hg,Os in Polystyrenes (44)	INAA
		Ni in solutions (10)	AA
H. Cooper	Safety Div.	NaCl Solutions (2)	AA
L. DeJonghe	M.S.E.	Na,Al,Si,Zr in Na-B-alumina (27)	INAA + AA + Color.
		Ca in solution (1)	WC
		Impurities in Mo & Na-B-alumina (3)	ES
G. W. Feigenson	Biochem.	Tb in solutions (2)	AA
J. Galloway	Ecology	Anal. of sediments (4)	INAA + RNAA
T. Gold	Space Sci.	Analysis of glass (1)	AA
G. G. Hammes	Chem.	Cu,Mn in solutions (7)	AA
J. Henderson	Anthrop.	Anal. of pottery (1) & obsidians (4)	ES + INAA

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MSC Analytical Facility Report for 7/1/75-6/30/76

Investigator	Dept.	Analysis (No. of Samples)	Methods Used
G. P. Hess	Biochem.	Tb in proteins (44)	INAA
		I in protein (1)	INAA
D. Holcomb	LASSP	W,Li,Na in bronzes (24)	AA + INAA
		Impurities in bronzes (3)	ES
		Au & Cs in alloy (1)	AA
I. Iwasaki	U. of Minnesota	Noble metals in rocks (5)	RNAA
J. Lemley	LASSP	Impurities in KBr (5)	ES
Monarch Machine Tools, Cortland, N.Y.		Analysis of steel (1)	AA
E. L. Muetterties	Chem.	Al,Cl,Cr,I,Ni,Br,Na,Hg,Zn,Fe in inorganic complexes (12)	INAA
M. Purchase	DEA	Al in cellophane-clay (47)	INAA
R. Raj	M.S.E.	Ca in Si_3N_4 (8)	AA
T. Rhodin	AEP	Analysis of Steels (2)	AA
A. L. Ruoff	M.S.E.	Impurities in TaC (3)	ES + AA
		Al in AlP (1)	INAA
F. R. Scholer	Chem.	Rh,B,Ni in compounds (4)	INAA + AA
D. N. Seidman	M.S.E.	Ni,Mo in wires (2)	WC + AA
		Au in Pt wire (1)	INAA
		Analysis of W.Re wires (8)	ES
M. F. Semmelhack	Chem.	Br in polystyrene (1)	INAA
M. J. Sienko	Chem.	V in Nb.V.Se comds. (16)	INAA
		NH_4^+ & W in amm. tungstates (18)	AA + WC
		Tl in Tl-tungstate (2)	AA
		Anal. of La.Yb & La.Eu compounds (6)	ES
		Impurities in WO_3 (1)	SSMS
		Heavy metals in amm. tungstates (5)	AA
		Impurities in Ta (1)	SSMS
		Anal. of W.Se,Nb.Se,Ta.Se alloys (8)	ES
R. Silsbee	LASSP	Fe in Cu.Fe alloys (15)	AA
R. Sundelin	Nuc. Studies	Impurities in NbC (1)	ES
C. L. Tang	E.E.	Anal. of Yb glass (1)	ES
J. R. Visalli, Tompkins County Health Dept.		Anal. of water (1)	AA + Color.

AA - Atomic Absorption Spectrometry; Color. - Spectrophotometry; ES - Optical Emission Spectrography; INAA - Instrumental Neutron Activation Analysis; RNAA - Radiochemical Neutron Activation Analysis; SSMS - Spark Source Mass Spectrometry; WC - wet chemistry.

2. New Problems Undertaken.

A large number of intermetallic compounds (67) were analyzed for Prof. Sienko by techniques of INAA, SSMS, ES and Wet chemical methods.

Prof. Purchase continued her analysis for Al in clay soiled cellophane samples (47) by INAA. Protein samples (44) tagged with traces of Tb were analyzed by INAA for Prof. Hess. Modified polystyrenes (44 samples) were analyzed for Sn, Hg, Os, Al, Cl and Br by INAA for Prof. Burlitch. INAA used in all these cases is particularly well-suited for these specific analyses. The same analyses by standard methods are either almost impossible to perform, or too time consuming.

Analysis of Na-B-aluminas (27 samples) continued from last year for Prof. DeJonghe as part of his project for development of better batteries. Analysis of a large number of W-bronze samples (24) for Prof. Holcomb also continued.

A few examples of unusual analysis include analysis of NaCl solutions for Cornell Safety Division. These materials were used in breaking open the vending machines on the campus by some students. Some obsidian samples (4) were analyzed for Prof. Henderson with a view to trace the trading patterns in pre-Columbian Mesoamerica. Lastly, a few yellow-green water samples from the vicinity of N.Y.S.E.G. Milliken Power Station were analyzed for Tompkins County Health Department. This water was found to have several hundred times excess over maximum allowable concentrations of Cr(VI). A field test was devised for the use of Tompkins County Health Department for checking Cr(VI) concentration in water wells of Lansing residents.

3. New Equipment Installed.

A new atomic absorption spectrophotometer, AA-6 by Varian, was purchased at the beginning of this progress report time period. Coupled with our M-63 Carbon Rod Atomiser, this instrument is proving very useful in obtaining precise data on metal concentrations in solutions.

A vidicon flame spectrometer, developed by Prof. Morrison's research group, is being used for multielement atomic flame emission analysis of solutions difficult to analyze by standard atomic absorption spectrometry.

R. A. Nadkarni
Research Manager.

MSC Computing Facility
Annual Report
July 1, 1976-June 30, 1976

During the year the Computing Facility became more and more focused on the multi-user system, although the hardware arrays which comprised the Facility in the past continued in operation. This report will review each of the three elements which make up this Facility.

(1) Multi-User System As the year began, we had received delivery of the hardware of the ModComp IV Computer System which was to be the central unit in a new multi-user system to serve the MSC community and some non-MSC chemistry and Applied Physics faculty. During the first quarter of the year, it became clear that ModComp would not be able to meet its commitments for operating system software, and we reluctantly decided to terminate the order and re-open the search for a satisfactory system. A Prime 300 was chosen and ordered, and system operations began in January. Rapid development of on-line connections to individual laboratories followed, as did the equipping of two "public" terminal rooms for the user community in Clark Hall and Baker Laboratory. By the end of June, the system had become a well-established, integral part of the laboratory computing operations of about 25 research groups.

A system of charges for connect time, terminal time, and CPU and disk use was established by the operating committee and resulted in the following income:

January	$ 480
February	1049
March	1393
April	1666
May	1583
June	1624

In addition, this unit of the Facility is the source for charges for interface development and construction and materials costs which amounted to about $1500 per month during the last half of the year.

(2) PDP-11/20 and GT-40 The PDP 11/20 computer system and GT-40 graphics terminal located in E-8 Clark Hall continued to be very actively used during the year, mostly by Clark Hall experimental groups. The GT-40 is mobile and can be wheeled to an experimental site in Clark during a run, or used in E-8. This unit of the Facility is also the clearing-house for billable time for system repairs by Jim Harman and applications programming by Rick Cochran. A summary of month-by-month hourly usage of the PDP 11/20, GT-40, and repair/programming service as billed is as follows:

	In Hours		
	PDP-11/20	GT-40	Repair/Programming
July 1975	393.5	70	—
August	251	88	89
September	154	120	100.5
October	147	175	52
November	208	144	160
December	169	102	40.5
January 1976	242	157	158.5
February	61	117	61
March	135	201	179.5
April	118	221.5	42
May	139	23	31.5
June	94.5	112.5	—
Year Total	2,112.0	1,531.0	941.5

It is probable that some of the work done in the past on the PDP-11/20 has switched and will switch to the Prime 300, and that the former will become dedicated to longer applications by single users, particularly the electron microscopy/energy analysis program of Professor Silcox.

(3) PDP-12 This computer system in Bard Hall serves research groups there, and has the advantage of an extensive although now somewhat obsolete, program library. Plans are underway to review the status of laboratory computing in the MSC groups in Bard and Thurston with the thought of possible MSC assistance in whatever the next step there might be.

Non-Metal Crystal Growing Facility

Annual Report for Year Ending June 30, 1976

Report Outline and Summary

I. Czochralski Growth
   a. Customers
   b. Special materials
   c. Special techniques

II. Other Projects
   a. Tungsten bronzes
   b. Arsenic chalcogenide glasses
   c. $(SN)_x$, a quasi one-dimensional superconducting polymer
   d. Vapor phase epitaxy of GaAs
   e. Deformation of calcite and olivine
   f. X-ray studies
   g. Crystal grinding and polishing

III. The Future

I

During the year 128 crystalline boules of alkali halides or divalent metal-containing halides were pulled from melts using the Czochralski technique. This corresponds to roughly twice the volume produced in recent years. Largely responsible for the increase was the demand from Professor Sievers group for crystals relating to the KBr laser window project. Twenty crystals were grown in response to orders from sources away from Cornell including Kernforschungsanlage Jülich, Atomic Energy of Canada, Limited (Chalk River), Naval Research Labora-

tory, Naval Surface Weapons Laboratory, University of Washington and Atomergic Chemetals Corporation. Most of the orders were for routine materials; however, in a continuation of a project begun last year for Atomic Energy of Canada, crystals of $K(Zn_{1-x}Mn_x)F_3$ with $x = 0.1$, 0.25, and 0.5 were successfully pulled.

At Cornell boules of $RbCoF_3$, $K(Co_{0.9}Zn_{0.1})F_3$, and $K(Co_{0.9}Ni_{0.1})F_3$ were grown for Professor Fitchen and several alkali halide crystals were pulled for Professors Maxfield and Ruoff.

Approximately a third of the Facility's annual production was related to the ARPA laser window project underway in the research groups of Professors Pohl and Sievers. A number of techniques were employed in efforts to examine and elucidate factors contributing to absorption of 10.6 micron radiation by KBr crystals. A series of attempts were made to purify further the starting salt by exposing it to bromine or carbon tetrachloride at temperatures in the vicinity of the melting point. Initial measurements obtained on crystals grown from bromine treated salt seemed promising, but have not proved reproducible, and thermodynamic analysis shows that bromine should not be expected to remove hydroxide from KBr. Similar analysis of treatment with CCl_4 indicates that hydroxide removal is energetically favored, however experimental difficulties leading to accumulation of carbon as pyrolysis of CCl_4 proceeds has thus far prevented systematic evaluation of the technique.

We have also attempted to examine the optical properties of KBr as a function of growth technique. Crystals grown from melts derived from previously pulled crystals are apparently indistinguishable from those grown straight away. Recently

obtained data does show that the rate of growth may be critical to optical perfection. Slowly pulled crystals (approximately 5mm/hr) appear to be superior to those grown at the usual rates (15 mm/hr). These preliminary results remain to be substantiated. Careful attempts to obtain highly polished damage free surfaces without cleaving has failed to provide crystals with significantly improved absorption properties.

In a separate project the research group of Professor Sievers has undertaken a spectrographic analysis of certain vibrational modes in 32 alkali halide boules containing complex anion dopants such as ReO_4^-, CrO_3Cl^-, SO_3F^-, ClO_3^-, BrO_3^-, and OCH_3^-.

II

A number of other projects were undertaken or continued in the Facility. Professor Holcomb's group continued to produce tungsten bronzes by electrolysis of tungstate melts in simple tube type furnaces. A postdoctoral fellow in Professor Sievers group is attempting to produce arsenic chalcogenide glasses of high optical perfection by heating the materials in evacuated quartz vessels. Presence of bubles within the glassy mass and fracturing of the quartz sample vessel during cooling are problems with which we are dealing.

Professor Pitchen's group has been studying the far infrared, infrared, and Raman characteristics of $(SN)_x$, a quasi one-dimensional superconducting polymer. Thin layers (0.1-1.0 microns) of the material are deposited from the vapor on substrates such as mylar, teflon, germanium, or KI which are mounted on and cooled by a water-cooled cold finger. At 150°C a source of

$(SN)_x$ vaporizes; polymer molecules are deposited in a one-dimensionally oriented layer. Only substrates having suitably matched lattice dimensions are possibilities and even then the deposited layer often adheres only poorly. Nevertheless, $(SN)_x$ has been successfully deposited on each of the above named substrates.

The relatively sophisticated vapor phase epitaxy system has reached the experimental stage. Professor Ballantyne's group is attempting to grow thin GaAs layers epitaxially on crystalline substrates. Early runs have occasionally resulted in desirable layers but more frequently no layer or an oxide layer has formed. Accordingly, it has been necessary to alter the detailed geometry of the system as well as the growth parameters and to search for leaks or defects in the purification system upstream from the reaction site. Experiments are continuing.

The Centorr high temperature resistance furnace is being used by members of Professor Kohlstedt's group to study the deformation and ultimately the dislocation density in calcite and olivine as a function of load in the vicinity of 1500°C. Iron ions migrate to the dislocation centers and are oxidized at 900°C. The resulting concentrations of color are distinguishable optically. The research is motivated by interest in geologic interpretations of natural specimens. Unfortunately persistent difficulties with Centorr hardware necessitated development of a substitute furnace with separate power supply. Only the water cooled "can" of the original furnace is now being used.

During the year the Facility manager has involved himself in the X-ray elucidation of materials produced by Professor Burlitch's students. The structure of $Co_4Zn_2(CO)_{15}$ was successfully completed. It is distinguished by Zn atoms bridging a Co–Co bond and also bonded to additional Co atoms. It is the only known example of Zn atoms bonded to as many as three other metal (Co) atoms. The molecular structure proved to be different in very significant ways from that predicted from spectroscopic and analytical data.

In a separate X-ray study of a chromium phosphinato-acetyl acetonate complex of interest to Professor Scott, it was shown that the material was not that expected. Whether or not the material is a distinct polymorph or structure of the same molecule, or something completely different remains to be determined.

The year's major addition to Facility equipment and capability is a Model 450 South Bay Technology crystal facing and lathing instrument. The instrument achieves highly smooth damage-free surfaces by allowing application of extremely light pressures between a polishing cloth mounted on a vertically rotating wheel and the rotating sample which is mounted on a delicate flexure or pendulum-like mechanism. The polishing is accomplished chemically, electrochemically, or by simple dissolution rather than by a grinding action. A variety of materials including bismuth, aluminum, silicon, tin, $(NH_4)H_2PO_4$, and alkali halides have so far been polished using a variety of etchants. The machine has been used by the groups of Professors Sievers, Maxfield, Balluffi, Ballantyne, and Batterman, as well

as by Facility personnel. Interest in the instrument and satisfaction with results seem to be spreading and recently the instrument has seen almost daily usage.

III

In the next year we will be striving to expand the grinding and polishing capabilities of the Facility in accordance with the needs of MSC members. We will soon be ordering a power supply for electropolishing applications in conjunction with the Model 450 facing and lathing instrument. Other grinding and polishing equipment presently available for use in the Facility include a South Bay Technology Model 850 slicing and dicing instrument, an acid saw, a horizontal polishing wheel and a variety of accoutrements.

Because of the history of problems associated with the Centorr furnace, it is hoped that it can be refurbished and updated so as to more satisfactorily meet its original specifications. An offer from Centorr to rework the furnace proper without charge has been received; Centorr will also modify at nominal charge the chamber in a desired fashion so as to permit effective separation of the heating element from the sample chamber; and several components including the vacuum instrumentation should probably be replaced as weill. When this is accomplished the furnace should be far more versatile and dependable.

A Trans-Temp Corporation two zone tube furnace has been ordered. It has gold films inside an outer pyrex jacket; these are transparent and allow rapid equilibration of the zones at up to 1000°C and also facilitate flat temperature profiles over 80%

of each zone's length. We hope to use it for growth of crystals by the Bridgman technique.

J. T. Lemley

MSC Electron Microscope Central Facility - Bard Hall

Annual Report

July 1, 1975 - June 30, 1976

Director of Facility: S. L. Sass

Facility Manager: R. Coles

Lab Technician: G. Ross

I. Clients Served

A. Transmission Electron Microscopy (TEM)

1. R.W. Balluffi - 8 users
   Structure of grain boundaries

2. S.L. Sass - 5 users
   (a) Structure of grain boundaries
   (b) Phase transformations in Ti and Zr alloys

3. L. De Jonghe - 4 users
   (a) Phase transformations in ceramics
   (b) Defect structure of oxides

4. D.N. Seidman - 6 users
   (a) Radiation damage
   (b) Shape of field-ion microscope specimen tips

5. H.H. Johnson - 2 users
   Deformation structure of iron and steel

6. E.J. Kramer - 4 users
   (a) Microstructure of polymer films
   (b) Epitaxial films

7. D. Ast - 3 users
   Amorphous materials

8. A.L. Ruoff - 2 users
   Ultra-fine grain carbides

9. D.L. Kohlstedt - 4 users
   Structure of carbides

10. R. Raj - 2 users
    Structure of silicon carbide

11. C.Y. Li - 1 user
    Deformation structure of metals

B. Scanning Electron Microscopy (SEM)

The projects are too many and varied to be easily summarized. Listed is the user and his department.

MS&E Users

1. Yetter
2. Krenitsky
3. Goodhew
4. Mancuso
5. Krenz
6. Schwartz
7. Quick
8. Chan
9. Putz
10. Wachob
11. DeJonghe
12. Herman
13. Unertl
14. Allender
15. Yohe
16. Shih
17. Schultz
18. Kohlstedt
19. Huang
20. Hsieh
21. Guan
22. Clemans
23. Nelson
24. J. OLeary
25. Natan
26. Lou

Other Users

27. Sundelin - Nuclear Stud.
28. Berenz - EE
29. Yang - EE
30. Sanda - Physics
31. Gupta - EE
32. Parthasarathy - CD&P
33. Warlaumont - AP
34. Tingey - Bot. & Ent.
35. Uhl - Botany
36. Kratzer - EE
37. Carson - M&AP Eng.
38. Sinclair - Plant Path.
39. Eickwort - Entamology
40. Boyce - M&AP Eng.
41. Ryan - EE
42. Basu - EE
43. Bird - Geology
44. Hoch - Plant Path. (Geneva)

II. New Projects Started This Year

A. TEM

1. R.W. Balluffi
   (a) High resolution study of the structure of high angle grain boundaries
   (b) Structure of near coincidence boundaries

2. S.L. Sass
   (a) High resolution study of defects in Zr-Nb b.c.c. alloys
   (b) Diffraction study of segregation to grain boundaries

3. D.L. Kohlstedt
   High resolution study of the structure of vanadium carbide

4. R. Raj
   Structure of silicon carbide

B. SEM

1. H.H. Johnson
   Hydrogen attack in low and high carbon steels

2. C.Y. Li
   Grain boundary cavitation and hydrogen attack in Ni

3. J. Blakely
   Topography of Zn cleavage surfaces

III. New Equipment

Thin film sputtering device.

IV. Summary of Microscope Use

Month	Microscope Use		Monthly Income (Machine time, labor, photographic plates)
	TEM	SEM	
July	208 hrs.	66.5 hrs.	$ 1784
August	248	51.75	1774
September	363	52.25	1708
October	345	88	4307
November	300	49	3026
December	160	74.75	1389
January	216	82.75	1969
February	196	72	2191
March	232	108	2763
April	160	76	1855
May	197	68.5	2055
June	269	88.25	2961
1975 - 1976	2,894 hrs.	877.75 hrs.	$27,782

In order to demonstrate how much the microscope lab use had increased over the past few years the appropriate information for the last two years is summarized below:

1974 - 1975	1,537 hrs.	893 hrs.	$21,507
1973 - 1974	1,181 hrs.	661 hrs.	$16,403

It is seen that the TEM use has increased by more than 85% in one year, while the SEM use has remained approximately constant. Even more impressive, it is seen that the TEM use has increased by more than 150% over two years ago.

V. Future Directions and Needs of the Lab

A. Space

There is an urgent need for additional space for the MSC EM lab. It is worthwhile reviewing the past development of the lab in order to gain perspective on its present and future needs.

Following the establishment of the MSC microscopy facility in Bard Hall in 1967-68, extensive renovations were carried out in the sub-basement in order to provide a home for the lab. In 1968 the new laboratory was quite spacious, since room was provided for 4 microscopes and at the time, there were only two microscopes. Since then the facility has purchased three new microscopes (two transmission and one scanning) and traded in one old microscope. Thus, the facility is now filled to capacity. As seen in Section IV the TEM use has increased by 85% in one year. It is worthwhile to note that the facility has been obtaining microscopes at the rate of one every 2 years since its establishment in 67-68. In 1972 a small area in SB60 was partitioned off for a high precision lathe and other necessary machine tools. Before the purchase of the Siemens 102, the research manager and lab technician could find office space in a room containing a "retired" microscope. As well, storage space was available in this room. In our current situation there is no office space available, and temporary quarters have been squeezed into one corner of the central lab room of the facility. We are also forced to store supplies in cabinets in the corridor outside of the lab. There are currently plans to request at least one new microscope for the facility. Clearly it is time to add additional lab space to the facility. The best solution would be to add one microscope room (16' x 12') and one large room (20' x 16') which would serve now as (1) an office for the manager and the technician, (2) an additional area for analysis of results, (3) storage space and (4) space for a small high precision machine shop. Temporary wooden partitions would be put up to separate the machine shop from the rest of the large room. If in the future a sixth microscope was added, the large room can be split into 2 rooms (16' x 10'), one of which would house the microscope, and the other would serve as cramped office space.

B. Equipment

During the past year a survey of the MSC membership was carried out to determine whether there was any interest in electron-optical instruments with microchemical capabilities. The results of this survey showed that there is a very strong interest in an <u>electron microprobe</u>, which is computerized and can do quantitative chemical analyses. A strong second preference was expressed for a <u>high resolution electron microscope with scanning transmission capability</u> which could give qualitative chemical analyses of thin foil specimens. This instrument would serve two purposes since it could take some of the load off the Siemens 102, the only high resolution instrument in the Facility, which is currently being used very heavily by 4 different research groups doing high resolution studies. A request has been submitted to the MSC for a computerized electron microprobe.

Report of the Electronics Facility
1975-76
Supervisor: D. R. Knettles

Summary of the Facility Program

The Electronics Facility supports MSC research basically through three modes of activity: repair, service and maintenance, and construction of electronics equipment. Over 1975-76 as in recent years, there was more emphasis on repair and service than on construction.

Repair work consists of trouble-shooting faulty equipment, finding the fault, and repairing it. Service work consists of routine maintenance, cleaning, lubricating and tuning or calibrating equipment as well as providing information to research workers on electronics resources such as sources of supply, known reliability of components, etc. Construction of new equipment is done from the client's curcuit drawing.

During 1975-76 a new time mark generator was purchased. This model TG 501 (Tektronix) unit has been integrated into our test console of Tektronix series 500 units for trouble shooting a wide variety of electronics equipment.

In addition to servicing research electronics equipment the technician continues two regular service commitments in Clark Hall. These are (1) maintenance of projection and public address systems on the seventh floor meeting rooms and (2) repair and service of instructional laboratory equipment on an emergency basis for the Department of Physics.

The technician keeps open channels of communication with the Computing Facility which has done a number of servicing jobs on computers and related circuitry in a number of MSC research groups.

During 1975-76, the following research groups, listed by faculty member, and facilities had work done by the Electronics Facility: (Number jobs in parentheses)

I. M.S.C. Members and Facilities

Chemistry

A.C. Albrecht (5)
S.H. Bauer (9)
J.M. Burlitch (1)
G.H. Morrison (3)
M.J. Sienko (2)

Applied and Eng. Physics

B.W. Batterman (2)
R.A. Buhrman (3)
R.K. Clayton (1)
T. Cool (16)
T. Rhodin (9)
B.M. Siegel (8)
W.W. Webb (20)

LASSP

R. Bowers-B. Maxfield (16)
R.M. Cotts (2)
D.B. Fitchen (2)
D.F. Holcomb (6)
H. Mahr (3)
R.O. Pohl (10)
A.J. Sievers (16)
R.H. Silsbee (1)
D. Lee-J. Reppy,
R. Richardson (28)

Other Engineering

R. McFarlene (3)
C. Tang (1)
G. Wolga (9)
W. Sachse (2)

Materials Science and Engineering

D.G. Ast (1)
J.M. Blakely (24)
H.H. Johnson (10)
R. Raj (3)
A. Ruoff (3)

MSC Facilities

Mech. Testing (3)
Materials Prep. (12)
T.O.L. (13)
Crystal Growing (4)
Laser (3)

II. Non-MSC Groups

LASSP Stockroom Loan Equipment (3)
LASSP PA System (2)
Physics Instructional (6)

Applied and Engineering Physics

A. Kuckes (8)

Plasma Studies

Humphries (13)
Sudan (1)

Chemistry

Elson (1)
Henion (1)

Biochemistry

Dunnan (4)
Roberts (1)

Mech. & Aero Engineering

DeBoer (1)
Gouddan (1)
Mahajan (1)
Skaukatullah (3)

Ag Engineering

Hashimoto (1)

L.N.S.

Tigner (1)

Pesticide Residue

Bache (1)

Low Temperature Facility
July 1, 1975-June 30, 1976

1. Clients served

a. Liquid Helium - Total liters sold - 23,100.25 liters

Total clients served - 69 plus

Low Temperature Labs., Clark Hall:

Professor	Clients	Professor	Clients
Lee		Bowers	4
Reppy	8	Fitchen	2
Richardson		Siegel	2
Webb	5	Hartman	4
Sievers	5	Mahr	2
Pohl	2	Sienko	4
Wolga	2	Holcomb	2
Silcox	3	Silsbee	3
Cotts		Cool	2

Baker Laboratory:

Porter	1
Sienko	2
Bauer	2

Bard and Thurston Halls:

Siedman	4
Kramer	2
Moon	2

Phillips Hall:

Wolga	3

Rockefeller Hall: Some liquid helium used to acquaint new people with liquid helium

Plant Science	1

b. Helium Gas - Helium Gas sold - 50,360 cubic feet - 219 tanks

Low Temperature Lab., Clark Hall: Helium Gas Consumption by Cylinders

Professor	Tanks Used	Professor	Tanks Used
Lee		Siegel	10
Reppy	26	Seidman	2
Richardson		Bauer	15
Webb & Buhrman	12	Morrison	4
Sievers	8	Cool	8
Pohl	2	Hartman	2
Wolga	14	Holcomb	3
McFarlane	8	Sienko	7
Bower	6	Silsbee	1
Cotts	1	Kramer	2
		Mahr	2
		Porter	2
		Rhodin	1
		Fitchen	1
		Scott	1

Facilities:

Technical Operation Laboratory	8	Tanks Used
Low Temperature Facility	45	"
Crystal Growing	1	"
Analytical Laboratory	2	"
Machine Shop	1	
Rockefeller Hall	1	
Space Science	3	
Newman Laboratory	24	

2. New Problems Undertaken: No problem at this time

3. New equipment or processes installed, or new services begun:

   a. Our new helium gas recovery line is installed and finished and working very well and so far have had very little problems with the line. We thought we might have trouble with large amounts of air getting into the line when our clients make their liquid helium transfer but so far very little air is getting in.

4. Some statistical measure of routine work performed:

   a. The main function of the Low Temperature Facility is to always maintain and adequate supply of liquid helium at all times to take care of our many clients here at Cornell and Ithaca College. This is done by buying our liquid helium which is put out for bid and on a three year contract and also by making it with our cryostats when the need arises.

b. We have a secondary function and that is collecting helium gases, cleaning and returning the gases back to our clients.

In addition to the above work the following is done:

1. Maintain day to day repairs on all liquid helium dewars used at Cornell. Maintain day to day repairs on our high pressure helium gas compressor and also on our low pressure compressor which runs our two cryostats. Also make all major repairs on above equipment.

2. Maintain repairs on our sixty seven (67) helium gas cylinders.

3. Design and layout all helium gas recovery line and help install and order all pipes, valves, gauges, and etc.

4. Design and layout all high pressure helium gas lines and help to install.

5. Give assistance to our clients in designing their liquid helium transfer tube and give instruction on the proper and safe way to use our liquid helium dewars and how to use the transfer line the first time.

6. Give assistance to our new clients on their first liquid helium transfer and also help out our regular clients when ever they need assistance.

7. Liquid helium sold for fiscal year - 23,100.75 ℓ.

8. 50 liter liquid helium dewars received and returned - 421

9. 100 liter liquid helium dewars received and returned - 72

10. 500 liter liquid helium dewars received and returned - 5

11. Liquid helium transfers - 1,522 .

12. Liquid nitrogen transfers - 3,358

13. Liquid nitrogen used in liquid helium dewars - 34,273 liters

14. Liquid nitrogen used in helium gas repurifier - 3,048 liters

15.

			Tanks
a. Helium gas collected by the Low Temperature Facility	77,310	Cu.Ft.	=336
b. Helium gas sold by the Low Temperature Facility	39,990	"	=174
c. Helium gas used by the Low Temperature Facility	10,320	"	= 45
d. Helium gas in subbasement storage	26,950	"	

16. Record day to day use of liquid helium from log books and helium gas.

17. Compile the monthly billing of liquid helium and helium gas for MSC.

18. Clean the weekly collected supply of helium gas each Thursday through our repurifier.

19. Everyday check all liquid helium dewars for ice blockage and fill liquid nitrogen jacket.

Materials Preparation Facility

The laboratory functions as a facility for the growth and preparation of metallic single crystals and purification of materials. Preparation of alloys their heat treatment and fabrication are also done in this laboratory.

* Clients Served by Name and Service

NAME		PROJECT	HOURS
Prof. D. Ast	i)	Machine and heat treatment of Glassy metals	25
	ii)	Zone refine iron specimens	8
	iii)	Vacuum melt and cast Pb-Bi alloys	10
	iv)	Vacuum melt Cu changes for 'E' beam gun	2
Prof. R. W. Balluffi	i)	Sputter etch silver specimens	10
	ii)	Set-up system for hydrogen annealing of NaCl bicrystals	8
	iii)	Design and build horizontal zone refiner and crystal growth unit	40
	iv)	Preparation of a 10% InAu alloy, roll into sheet - Preparation of a 5% InAu alloy, roll into sheet	4
Prof. J. M. Blakely	i)	Preparation of Ni single crystals for LEEDS experiments Oriented crystals (110), (111) and (100) were used, these crystals were cut, polished and slopped with carbon	160
	ii)	Zone refine Mo rods Zone refine Ta rods Zone refine W rods for use as LEEDS crystal holders	20
	iii)	Growth of Pt single crystals, orient, cut, polish into LEED type specimens.	20
	iv)	Growth and preparation of high purity Zn single crystals. Set-up apparatus for growth of ZnO single crystals.	20
	v)	Purification of nickel by reactive gas and Zone refining.	40

NAME		PROJECT	HOURS
Prof. L. DeJonghe	i)	Build gas inlet manifold	3
	ii)	Set-up hot press unit to be used in conjunction with Radio Frequency induction systems.	2
	iii)	Sinter powders	4
	iv)	Design and build furnace system for thermo balance	24
	v)	Calibration of optical pyrometers	4
Prof. H. H. Johnson	i)	Sputter Pd-Fe and Nb on to different substrates	60
	ii)	Heat treatment of Powder metallurgy samples	40
	iii)	Zone refine Ferrovac 'E' bars	25
	iv)	Carburize Ferrovac "E" specimens	10
	v)	Zone refine Nb rods, roll into sheet form and degas by heat treating in ultra high vacuum of 2×10^{-10} μm Hg	12
	vi)	Spark machine thin specimen for examination in the electron microscope.	20
	vii)	Design and build two high pressure (2200 psi) high temperature (800°C) pressure bombs	80
	viii)	Growth of Fe single crystals by thermal cyclicing techniques	20
	ix)	Make Fe 2.9 w% Si alloys	5
	x)	Heat treatment of iron and steel alloys in vacuum, hyrogen Oxygen etc.	180
	xi)	Design and build special apparatus to use R.F. unit and residual gass analysiser	
Prof. C-Y. Li	i)	The growth of Al single crystals oriented (111), cut, and machine into tensile specimen.	200
	ii)	Heat treatment of 270 Grade Ni both in high pressure hydrogen and vacuum.	170
	iii)	Develop system for the growth of stainless steel single crystals.	70

NAME		PROJECT	HOURS
Prof. Li (con't)	iv)	Heat treatment of Iron samples - growth of Iron crystals by the strain anneal method.	25
Prof. A. L. Ruoff	i)	Sputter SiC thin films	20
	ii)	Heat treatment of steel rings of 4340 steel and maraging steel	40
	iii)	Wafer lava stone sheets with diamond wafering unit	125
	iv)	Vacuum Degas TiC specimen at high temperatures (1000°C) in $2x10^{-6}$ mm Hg vacuum	15
	v)	Spark machine tungsten carbide pistons	20
	vi)	Micro polish Silicon surfaces	10
	vii)	Heat treatment (normalize, soak, quench and temper) 1080, 4340 steels.	20
	viii)	Preparation of thin samples of TaC	10
	ix)	Growth of silver single crystals	8
	x)	Arc melt and cast cerium-zone refine cerium metal.	35
Prof. D. Kohlstedt	i)	Machine Mo rods and tungsten inserts - press fit inserts.	5
	ii)	Cast and Machine and set of lead weights.	8
	iii)	Spark machine carbide crystals.	4
	iv)	Spark machine tungsten crucibles with lids.	4
	v)	Vacuum anneal carbide crystals (VC .84) 1100°C in vacuum spark machine thin discs.	12
Prof. R. Raj	i)	Arc Cast and Roll Copper 0.15% Si alloys. Heat treatment of above alloy under oxidizing conditions.	14
	ii)	Preparation of a series of Cu-Si alloys and draw into wire.	40
	iii)	A distallation of a 5KVA lapel radio frequency induction heating unit-complete trial runs, build table for same.	8

NAME		PROJECT	HOURS
Prof. E. J. Kramer	i)	Vacuum and thermal treatment of plastic specimens.	200
	ii)	Collagen project	100
	iii)	TiG welding of Al	4
	iv)	Design and build freeze drying unit	30
	v)	Ultra high vacuum degas of 10% Mo-Nb alloy at $1x10^{-9}$ torr at 1800°C.	20
Prof. S. L. Sass	i)	Arc cast Zr-20% Nb alloy, grow of a single crystal - x-ray orient and spark cut a (111) oriented disc.	9
	ii)	Arc cast a series of Al-Cu alloys to be used as standards for the S.E.M.	6
	iii)	Silver solder x-ray jig.	1
	iv)	Sputter etch gold films	10
	v)	Preparation of Zr-13% Nb - Zr-14% Nb foil	4
Prof. D. Seidman	i)	Preparation of $MoNi_4$ wire, heat treatment of same	25
	ii)	Wire drawing of FIM alloys into .005 wire	60
	iii)	Spark machine MoTi wire for FIM specimens	20
	iv)	Zone refine Mo rods and grow oriented (110) single crystals from same.	8
	v)	Heat treatment of NiMg wires	4
	vi)	Preparation of high purity Iron wires.	10
	vii)	Preparation of 0.1% AuPt and 0.6% Au-Pt wire of .008" diameter.	10
Prof. B. Batterman	i)	Leak check high voltage x-ray machine, condition vacuum system.	4
	ii)	Spark machine Nb alloys	1
Prof. Cotts		Ultra high vacuum annealing of Nb foil at 1800°C for 8 hrs at $1x10^{-9}$ torr.	20
Prof. Mahr		Micro polishing of CdSe, CdS and lithium iodate single crystals.	8
Prof. D. Lee		Arc cast $PrNi_5$, heat trent under high pressure hydrogen, grind into powder	8

NAME	PROJECT	HOURS
Mr. B. Maxfield	i) Growth of oriented tungsten single crystals	6
	ii) Growth of 2" diameter - 8" long Al single crystals (110) orientation along the growth axis.	10
Prof. J. Silcox	Preparation of Al single crystals	2
Prof. Silsbee	i) Set-up arb ion system for production of thin films	8
	ii) Preparation of Fe-Pd alloys	2
	iii) Preparation of Ni-Fe alloys	2
Prof. T. Rhodin	i) Growth of Fe single crystals by the strain anneal technique. Preparation of LEED crystals of (110) and (100) orientations.	40
	ii) Preparation of Ni LEED crystals.	10
Mr. Padamsee	Sputter Nb thin films sputter Nb-TiN, NbN films on to R.F. cavities.	40
Prof. Holcomb	Drill .010" holes through carbide single crystals	2
Prof. Sienko	Fabricate molybdenum crucible and lid, designed to be electron beam welded	2
Mr. H. Aderhold	Fabricate of Indium and Cadmium sheet for use in Ward reactor.	6
Prof. Morrison	Preparation of Ti-Cu, Al-Fe, Ni-Ti and Cu-W alloys	8
Prof. Sachse	Fabrication of Al powder samples and heat treatment of same.	6
Prof. Wolga	Cast lead rediation sheilds	8
Prof. McFarlane	Micro polish ceramic crystals.	4

MECHANICAL TESTING FACILITY

This laboratory provides tensile, compressive, and cyclic loading machines for uni-axial testing and bi-axial testing. Some cryogenic and elevated temperature apparatus is available as well as many room temperature fixtures.

1) Clients Served by Name and Service

Prof. Ast	Cyclic loading of annealed iron based metallic glasses to study their fatigue behavior.
Prof. Balluffi	Controlled bending of NaCl crystals in solution to given radii of curvature
Prof. DeJonghe	a) Provided calibration weights for load cell b) Compressive testing of Sodium β alumina
Prof. Johnson	a) Strain annealing of Fe crystals b) Designed pressure vessel for use with hydrogen c) Cryogenic fracture of Fe and design and construction of grips for this.
Prof. Kohlstedt	Design help and loan of calibration equipment and LVDT's for strain measurement.
Prof. Kramer	a) Experiments to determine mechanical properties of reconstituted collagen hollow fibers. b) Experiments to grow n-heptane crazes in polystyrene at cryogenic temperatures. c) Room temperature fracture mechanics testing of crazes grown at low temperatures.
Prof. Li	a) Fracture experiments on notched Ni specimens. b) Load calibration of stress relaxation apparatus. c) Mechanical design help with new high temperature stress relaxation apparatus.
Prof. Raj	a) Modified and assembled torsion pendulum apparatus for measuring grain boundary sliding viscosity. b) Provided Instron for high temperature testing of Cu, Al, and stainless steel and aid with design and construction of these fixtures. c) Provided Instron and design help for construction of environmental chamber for crack propagation in adhesive layers. d) Preliminary design work on high vacuum high temperature furnace for MTS. e) Designed and supervised construction of die set and grips for use with 50klb MTS and RF heating system to be used for creep/fatigue experiments on stainless steel.

Prof. Ruoff	a) Measured electrical resistance changes with carbide anvils. b) Measured deformation of silicon and of tungsten carbide with diamond anvil.
Prof. Sachse (TAM)	Provide Instron for ultrasonic pulse sepctroscopy measurements.
Prof. Scott (Agr. Eng.)	Provide load cell and grips for tensile testing.
Prof. Taylor (Op. Res.)	Multi-filament load carrying study.
Mr. La Londe (NAIC)	Strength analysis of different end terminations for non-metallic cable.
Prof. McGuire (CEE)	Strength testing for concrete reinforcing wire.
Prof. Wang (Mech. & Aero.)	Strength tests on ultra-sonically welded ABS plastic and force measurement on welding apparatus during welding process.

In addition to research activities very limited educational uses were made of facility equipment and personnel.

Materials Science and Engineering - Technical aid has been given for the design and construction of new apparatus for the undergraduate labs. Two lectures were given to a mini-course on mechanical testing and the design of equipment for research.

Mechanical and Aerospace Engineering - Instron #3 has been used as part of an undergraduate lab to determine strength, modulus, and hardening properties of steel.

2. Routine Work Performed

A. MTS Usage

Prof. Ast	41%
Prof. Kramer	39%
Prof. Johnson	18%
Prof. Raj	1%
Prof. Li	1%
	100%

B. Instron Usage

Prof. Ast	32%
Prof. Kramer	22%
Prof. Ruoff	16%
Prof. Johnson	14%
Prof. Wang	7%
Prof. Sachse	3%
Prof. Raj	1%
Other	5%
	100%

Report Preparation Facility

Annual Report
July 1, 1975-June 30, 1976

One hundred ninety journal-type reports and twenty theses issued as MSC reports were processed through the Facility during the year and their abstracts published in the four issues of the MSC "Quarterly Report" which is sent to about 300 addressees. The use of an outside drafting service continued, with the Facility acting as the collection and billing point for drafting work — over 2000 fugures were drafted during the year through this system. Duplicating by the Facility continues to be done on the Xerox 7000 copier which has capabilities to reduce oversize figures or computer printouts to standard page size.

Annual Report
Technical Operations Laboratory (TOL)
July 1, 1975-June 30, 1976

Jobs were performed during the year for nearly every active MSC experimental group and for some non-MSC Cornell clients and a few outside groups. A list of the sorts of jobs done is as follows:

1. SnO_2 Coatings
2. Vacuum Furnaces
3. Grinding of Glass
4. Annealing of Metals, etc.
5. Sintering of Cu
6. Silvering Dewars
7. Bake-outs
8. Plating
9. Evaporations
10. R. F. Brazing
11. Electron Beam Brazing
12. Baking of Lava Parts
13. Rejuvination of Photomultipliers
14. Cleaning and Repairing of Vaccum Pumps
15. Building Finnegan Solid Probe
16. Machine Parts
17. H_2 Furnace Runs

The lab continued its "open door" philosophy, allowing experimentalists access to TOL tools and equipment in the shop, along with advice when needed, and continued to loan out certain equipment on a sign-out basis.

ANNUAL REPORT

July 1, 1975 - June 30, 1976

X-Ray Diffraction and Metallography Facilities

Facility Director - Professor B. W. Batterman
Research Manager - Don Bilderback
Research Specialist - Margaret Rich

X-Ray Facility - 315 Bard Hall

Clients Served:

50% from the Department of Materials Science and Engineering, 50% from other departments including Chemistry, Physics, Electrical Engineering, Theoretical and Applied Mechanics, Design and Environmental Analysis, Chemical Engineering, Applied Physics, Veterinary Anatomy and Geology.

Number of Individual Users: 50

MSC Accounts: 22

Other Accounts:
(ERDA, NASA, NSF, AF, GE, etc.): 28

Service Diffraction Tube Hours	MSC Accounts	Other Accounts	Total
Diffractometer, single crystal orientation	131.1	100.0	231.1
Transmission and back reflection Laue, Berg Barrett & Debye Scherrer	336.8	112.6	449.4
Small Angle Scattering	462.5	1655.3	2117.8
Fluorescence	127.1	75.0	202.1
TOTAL	1057.5	1942.9	3000.4
Rigaku Rotating Anode 2 users(7/75-6/76)			5386.0

X-Ray Facility - G12 Clark Hall

Clients Served:

Chemistry, Applied Physics, LASSP, EE, SAEP

Number of Individual Users: 20

MSC Accounts: 5

Other Accounts:
(ERDA, NASA, NSF, AF, GE, etc.): 15

Service Diffraction Tube Hours	MSC Accounts	Other Accounts	Total
Diffractometer, Transmission & Back Reflection Laue, single crystal orienter	60.4	212.0	272.4

Metallography Facility - 347 Bard Hall

Clients Served:

Materials Science and Engineering (50%), 50% from other departments including Chemistry, Physics, Electrical Engineering, Theoretical and Applied Mechanics, Geology, Mechanical Engineering.

Number of Individual Users: 158

MSC Accounts: 59

Other Accounts
(ERDA, NASA, NSF, AF, GE, etc.): 99

Service (Hours)	Total
Specimen Preparation (cut off wheels, rough grinding equipment, polishing wheels, specimen mounting, etc.)	694.8
Darkroom (enlargers [Omega, Log E, Beseler] dryer, chemical processing, etc.)	1048.0
Microscopes (Leitz, Reichert, B&L, Zeiss)	625.6
Photograpic Equipment	438.2
TOTAL	2806.6

Facility personnel time, in terms of percent working time is as follows:

75% - Instruction of individual users in diffraction, metallographic and photographic techniques, guidance in equipment operation and specimen preparation, consultation regarding projects to be undertaken utilizing facility equipment and accessories.

15% - Service work performed strictly by facility personnel.

10% - Instrumentation and maintenance, ordering supplies, facility records and work orders.

New Equipment and Services

1. The facility purchased a Kodak Ektamatic Processor which allows the researcher to take measurements, etc. from a stabilized print 15 secs. from negative exposure. The print can then be discarded or may be fixed, washed and dried in the usual manner for permanence. The processor has made it possible to schedule darkroom time more efficiently.

2. A new lithium drifted silicon x-ray detector has been purchased for use in qualitative fluorescence analysis. When coupled to our vacuum spectrometer, the detector can detect the presence of any element in the periodic chart from sodium (z=11) down thru the heavier elements. The detector has a resolution of 155eV and 5.9keV and can clearly distinguish adjacent elements in the periodic chart. Samples with a composition of just several elements can be analyzed in a matter of minutes.

Clark Hall

The X-ray and Metallography (Don Bilderback) and the Crystal Growth Facility (John Lemley) have arranged equpment for the cutting and polishing of crystals. A single crystal may be x-ray oriented and then simply transferred to a saw for cutting. Grinding and polishing equipment is also available to complete the specimen preparation. The following is ready for use:

	Equipment	Location
a.	Laue cameras for x-ray orienting, both Polaroid and wet film, can achieve 1^{o} accuracy	X-ray Facility
b.	Single crystal orienter, for achieving an orientation accurate to $.1^{o}$ or better	X-ray Facility
c.	South Bay string saw that accepts our orienting jigs	Crystal Growth Facil.
d.	South Bay Facing and Lathing Instrument	Crystal Growth Facil.
e.	Glass plate with SiC grits 400-3200	Crystal Growth Facil.
f.	8" polishing wheel for use with diamond paste	Crystal Growth Facil.
g.	Diamond wheel saw for precision wafering and general cutting of hard materials	TOL

Multiwire Detector Project

1. Just recently, the technology of building multiwire proportional chambers for High Energy Physics has been applied to the construction of area detectors for x-ray diffraction. A crossed set of x and y wire planes can be used to determine the position of detected x-ray photons on the face of a large (28cm x 28cm) area detector. With an effective number of wires per direction of 210 x 210, the x and y coordinates can be partitioned into 1.3mm segments. The processing electronics can give x and y coordinates in analog form for display on an x-y oscilloscope and in digital form for storage in a computer. The individual wires (several hundred in each plane coupled to delay lines) function somewhat like single wire proportional counters and hence it is possible to make a detector with energy resolution and a high quantum detection efficiency ($\sim$60% for Cu Kα radiation).

   We have undertaken a joint project with Professor Sass' group to build such a detector for imaging weak diffraction effects arising from grain boundaries in Au bicrystal specimens. Presently, the x and y wire planes are being fabricated in Neumann Laboratory using the facilities involved in building crossed wire chambers for the Wilson Synchrotron.

2. We are planning to arrange a second multiwire detector to display a Bock Reflection Laue images on an x-y oscilloscope. Therefore it would be possible to orient single crystals in real time without having to take several 10 to 15 minute photographs per crystal. Other real time displays of diffraction patterns might be possible if sufficient intensities are available.

3. Further use of the position-sensitive wire detectors will be probable in low angle scattering experiments now carried out in the X-ray Facility.

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